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Established in 1950, Photographic Science and Technique is prepared under the editorial management and control of the Technical Division of the Society. The first four volumes were issued as Section B of the PSA Journal and numbered 16B to 19B inclusively. As a separate publication, Series II, Volume 1, Number 1 started in the first quarter of 1954.

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PSA Technical Paper Award for 1954

Norman C. Lipton*

THE PSA TECHNICAL PAPER AWARD for 1954, given to the author or authors of the best technical article appearing in any official publication of the Society during each calendar year, was bestowed upon Lester Horwitz for the paper, "Mechanisms of Color Sensitization" published in the May 1954 issue of Photographic Science and Technique. Dr. Horwitz was a senior research assistant at Ansco at the time his paper was offered for publication. He has since joined the Midwest Research Institute in Kansas City, Missouri.

The inter-division award committee, working under the sponsorship of the Technical Division, awarded an Honorable Mention to A. A. Rasch and J. I. Crabtree, FPSA, of the Kodak Research Laboratories for the runner-up paper in the committee voting: "An Inorganic Developer Reactivated by Electrolysis", published in the same May 1954 issue of Photographic Science and Technique. The awards committee consisted of John A. Maurer, APSA, of MPD, W. K. Raxworthy, APSA, of CD, and John W. McFarlane, FPSA, Lloyd E. Varden, Hon. PSA, and Chairman, Norman C. Lipton, FPSA, of the Technical Division.

Formerly known as the *Journal Award*, this formal recognition of the outstanding technical paper published in each calendar year was instituted in 1949. Following are the respective authors honored in years past:

1949—J. I. Crabtree, FPSA: "Rapid Processing of Films and Papers" PSA Journal Vol. 15, pp. 130–136, Feb. 1949

1950—F. B. Noel, FPSA and P. B. Davis: "New Low-Voltage Low-Power Flashtube of High Efficiency" PSA Journal Vol. 16B (PS&T): pp. 11–16, Jan. 1950

1951—L. A. Jones, Hon. FPSA: "Psychophysical Evaluation of Quality of Photographic Reproductions" PSA Journal Vol. 17, pp. 751–764, Dec. 1951

1952—R. W. Henn, FPSA, "Properties of Developing Agents II. Paraminophenols" PSA Journal Vol. 18B (PS&T), pp. 90–95, Oct. 1952

1953—F. V. Chu, R. W. Nottorf, and W. H. Vinton: "Swelling Characteristics of Synthetic Polymer Emulsions Under Processing Conditions" PSA Journal Vol. 19B (PS&T) pp. 43–47, May 1953

Twelve papers in all were nominated by the committee members for consideration for the 1954 top award. These were scored by the committee on the basis of five factors weighted as follows: Technical merit, 20; importance of material, 25; originality of work, 20; breadth of interest, 15; and excellence of presentation, 20.

The regulations governing the Technical Paper Awards Committee appear on page 9 of the Administrative Practices for the Technical Division of the Photographic Society of America, approved by the PSA Board of Directors, October 6, 1954. Section 5 Article IX of the regulations prescribes that they be published annually in the PSA Journal but they are published here instead.

Sec. 2.: (*b*) *1. The TECHNICAL PAPER AWARDS COMMITTEE* shall consist of a Chairman, two members appointed by the Technical Awards Committee Chairman, subject to approval by the TD Chairman and by the TD Executive Committee, and one representative from each of the following Divisions other than TD who wish to participate: Color, Motion Picture, Nature and Stereo.

2. *Duties:* Its duties shall be to recommend to the TD Executive Committee the author or authors of the best technical paper published in the PSA Journal, Photographic Science and Technique or any other official PSA publication, to receive the Division's Annual Technical Paper Award.

3. *Award:* The PSA-TD Technical Paper Award shall be made on the basis of the following qualifications:

a) The paper shall have been published originally in any official PSA publication, during the preceding year.

b) The paper must deal with some scientific or technical aspect in the field of photography.

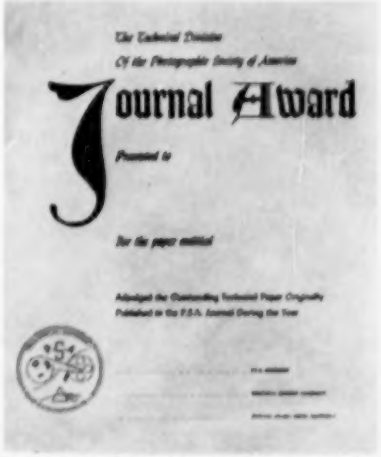
c) In judging the merits of the paper, three qualities shall be considered, as follows:

1. Technical merit and importance of material..... 45%
2. Originality and breadth of interest..... 35%
3. Excellence of presentation of material..... 20%

A majority vote of the entire Committee shall be required for the election of the Award. Absent members may vote in writing. The report of the Committee shall be presented to the TD Executive Committee before March 1st of the succeeding year. At the annual meeting of the PSA a suitably embellished certificate shall be presented to the author, or to each of the authors, of the most outstanding paper.

4. *Honorable Mention:* Other papers may be cited for Honorable Mention at the option of the Committee, but in any case shall not exceed three in number.

5. *Publication:* These regulations, a list of all Technical Paper Award recipients, the year of each award, and the title of the papers, shall be published at least annually in the PSA Journal. In addition, the list of papers selected for Honorable Mention shall be published during the year current with the award.



The PSA Technical Division diploma awarded annually to the author of the best technical paper to appear in an official publication of the Photographic Society of America.

* Chairman, Technical Paper Awards Committee, PSA Technical Division. Received 30 September 1955.

THE EFFECT OF VARIOUS PRETREATMENTS ON THE REACTION OF HYDROGEN PEROXIDE WITH A SILVER IMAGE*

G. W. Luckey, T. H. James, and W. Vanselow

ABSTRACT

Andresen found that when a developed photographic image was treated with a hydrogen peroxide–hydrochloric acid bath, the densest areas were attacked first, with a gradual dissolving of all gelatin in which developed silver particles were imbedded. This process, with subsequent modifications, has been used to make gelatin relief images.

The authors used a simple method to study the effect of various factors on the rate of decomposition of hydrogen peroxide by developed silver. A disk cut from uniformly exposed and developed film is immersed in the hydrogen peroxide solution and the time required to accumulate enough oxygen to float the disk is measured. The length of this time is inversely proportional to the peroxide concentration in the range from 4 to 33 percent. The time decreases exponentially with increasing temperature between 0 and 65 C. The apparent activation energy of this induction period is 12–13 kcal/mole for untreated developed film and is largely unaffected by treatments such as bathing in silver nitrate or potassium bromide. The length of the induction period decreases with increasing optical density of the silver deposit. The induction time is largely independent of the pH of the pretreatment solution in the range between 4 and 13. Pretreatments with potassium cyanide, sodium thiosulfate, and silver ions decrease the induction period, but it becomes independent of silver-ion concentration below 10^{-3} *M*. Formaldehyde hardening of the emulsion increases the induction period. Treatments with thioureas or selenium toning likewise increase it. The mechanism of decomposition of the peroxide and its action on the gelatin are discussed.

In 1899, Andresen[1] reported that "by the action of hydrogen peroxide on the silver image produced in gelatin, the densest parts are attacked first, and in such a way that from the surface of the film there appears a gradual dissolving of the silver with the gelatin in which the silver particles are imbedded." It was pointed out that the images thus treated show a marked relief, and that a 3 percent solution of hydrogen peroxide and 2 percent hydrochloric acid should be used for best results. Lüppo-Cramer[2] suggested that nascent oxygen formed in the decomposition of the peroxide causes the oxidation of the gelatin, making the latter more soluble. This technique has been reviewed by Wall[3] and Centa.[4]

The catalytic action of silver on the decomposition of hydrogen peroxide has been known for some time. Earlier studies have been reviewed by Bredig,[5] Berkman, Morrell, and Egloff,[6] Baxendale,[7] Abel,[8] and Weiss.[9,10] Bredig,[11] McIntosh,[12] and Wiegel[13] made quantitative studies of the catalysis by colloidal metals and showed that colloidal silver decomposes hydrogen peroxide in acid or neutral solution until the silver dissolves. When the solution is basic, relatively little silver dissolves. Light in the wavelength region above 4000 A does not influence the reaction, and the rate in neutral or alkaline solution is first-order with respect to hydrogen peroxide concentration.[5,12]

The mechanism of the decomposition has been considered by Weiss[9,10] and Abel,[8,14] who based their explanations on the Haber-Weiss chain mechanism for hydrogen peroxide decomposition.[15] In neutral solution, the primary process is

$$H_2O_2 + e_{metal} = OH + OH^- . \quad (1)$$

In alkaline solution, this is supplemented by the reaction,

$$HO_2^- + H_2O_2 = HO_2 + OH^- + OH. \quad (2)$$

The HO_2^- ion is produced by ionization of the hydrogen peroxide. A number of secondary processes have been suggested. Weiss favors the reactions,

$$H_2O_2 + OH = H_2O + HO_2. \quad (3)$$

$$Ag^+ + O_2^- = Ag + O_2. \quad (4)$$

$$Ag + HO_2 = Ag^+ + HO_2^- . \quad (5)$$

$$Ag^+ + HO_2^- = Ag + HO_2. \quad (6)$$

Abel suggests the reaction,

$$HO_2 + OH = H_2O + O_2. \quad (7)$$

Silver ion will catalyze the reaction by preventing chain termination and solution of the silver. Under the conditions of the present investigation, it seems probable that the rate-limiting process is represented by Equation (1). The secondary processes will have some influence on the rate of solution of the catalyst, and consequently on the rate of oxygen evolution.

The purpose of the present investigation is to study the effect of various pretreatments on the Andresen reaction and to learn whether the Weiss-Abel mechanism accounts for the observations.

Experimental

Several types of emulsion were used for this study: a paper emulsion, *A;* Eastman Fine Grain Release Positive Safety Film, Type 5302, *B;* and Eastman High Contrast Positive Safety film, Type 5363, *C*. The hydrogen peroxide was Baker and Adamson Reagent Grade. The

* Communication No. 1738 from the Kodak Research Laboratories, Rochester 4, New York. Received 28 July, 1955.

concentration of the solution was determined by titration with potassium permanganate solution and was between 30 and 33 percent. The usual concentration was about 33 percent.

Emulsions *B* and *C* were exposed and developed in Kodak Developer D-16 to the desired density. They were then fixed in Kodak Fixing Bath F-5 and thoroughly washed in distilled water. Emulsion *A* was exposed and developed in 1:1 Kodak Ektonol Developing Agent, fixed in Kodak F-5, and thoroughly washed in water. The temperature of the solutions was measured with a calibrated mercury thermometer. The reaction times were measured with a Gallet decimal stopwatch or with a Precision Scientific Co. No. 9230 Electric Timer. The pH of the various solutions was measured with a glass electrode.

Since the results did not depend on the size or shape of the sample, uniform-size squares or disks were punched from the strips of film to facilitate handling. In some of the work, the samples were squares, 0.8 cm on an edge. In the remaining experiments, the samples were disks, $^3/_4$ inch in diameter. The samples were immersed in hydrogen peroxide solution and, after an induction period of variable length, the peroxide decomposed catalytically at the emulsion surface, causing extensive gas evolution. Emulsion *A* was coated on paper, and the induction period was determined by measuring the time necessary for complete coverage of the surface with gas bubbles. Emulsions *B* and *C* were coated on cellulose acetate–butyrate film base. The gas bubbles produced in these samples at the end of the induction period adhered to the gelatin and lifted the disk to the surface of the peroxide solution. The time required for coverage and floating was perfectly reproducible, provided the concentration of the peroxide solution, the temperature, the emulsion, and the treatment before immersion were the same. As a result, the test provided a rapid quantitative method for studying the effects of various addenda and conditions on the induction period of the reaction of hydrogen peroxide with a layer of finely divided, gelatin-coated silver. As will be shown subsequently, this flotation method fails when the pH of the pretreatment solution is below 4.

Experimental Results

For silver concentrations corresponding to a density range between 0.6 and 2.0, the induction period is inversely proportional to the developed density. At higher densities, the period is probably determined by diffusion; at lower densities, the bubbles detach from the emulsion before floating occurs. Unless otherwise stated, the developed density of the samples used for these experiments was 0.86.

The length of the induction period is usually inversely proportional to the hydrogen peroxide concentration. Some immersion treatments cause large deviations from this relation, however, so that no general law can be stated. In the following experiments, the concentration-dependence follows inverse proportionality unless otherwise stated.

The effect of pAg was examined by immersing the disks in solutions of silver nitrate, potassium bromide, and potassium iodide. The disks were dried in air, then placed in the peroxide solution as before. The results

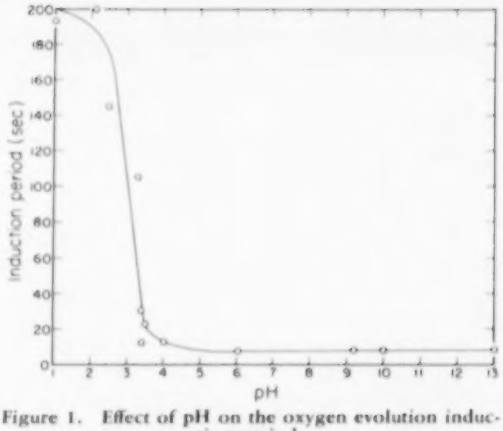


Figure 1. Effect of pH on the oxygen evolution induction period.

are summarized in Table I. The immersion in 0.001 *M* silver ion causes a seven-fold decrease in the induction period. Above this concentration, a further increase has little or no effect. This increase in rate caused by silver ions has been reported by Lüppo-Cramer.[2] Immersion in a 0.01 *M* solution of either potassium bromide or potassium iodide increases the induction period by about a factor of 4. The effect of the latter compound is complicated by its catalytic action.[7] The inhibition by bromide ions has been reported by McIntosh.[12]

Table I

EFFECT OF pAg ON THE INDUCTION PERIOD OF TYPE 5302 FILM EMULSION AT 1 C

Solution Description	Induction Periods in Seconds in 33% H_2O_2	16.5% H_2O_2	8.25% H_2O_2
(1) 0.01 *M* Silver nitrate	...	4	10
(2) 0.001 *M* Silver nitrate	...	4	10
(3) 0.0001 *M* Silver nitrate	9	24	47
(4) Untreated No. 5302	9	29	70
(5) 0.01 *M* Potassium bromide	51	125	237
(6) 0.01 *M* Potassium iodide	46	120	214

To test the effect of pH, disks were immersed in solutions of known pH and dried in air. The induction period after immersion in peroxide is independent of the pH of the pretreatment in the range extending from 4 to 13. Below pH of 4, the induction period increases with decreasing pH until a value of 2 is reached. Below this, the induction period is again independent of pretreatment pH. These results are plotted in Figure one. The low rates obtained with the acid-treated samples do not signify a decrease in the rate of attack of the peroxide on silver. Under these conditions, the silver is visibly attacked before the disk floats, and the attack is quite apparent in areas where no oxygen bubbles form. Samples which are pretreated in water show much less attack. Furthermore, the oxygen bubble formation on the surface of the acid-treated samples is a gradual process in contrast to the rather sudden build-up of bubbles at high pH.

When the pH of the hydrogen peroxide solution is increased by the addition of sodium hydroxide, the induc-

Table II

EFFECT OF SELENIUM TONING ON THE INDUCTION PERIOD OF TYPE 5302 EMULSION AT 23 C

Sample Description	pH	Induction Periods in Seconds in 33% H_2O_2	16.5% H_2O_2	8.25% H_2O_2
(1) Se toning, unwashed	2.0	34	93	350
washed	2.0	65	175	480
unwashed, incubated.	2.0	2000	...	...
washed, incubated.	2.0	300	1400	1830
(2) Se toning, unwashed	3.0	25	77	300
washed	3.0	110	...	...
unwashed, incubated	3.0	500	1800	...
washed, incubated.	3.0	875	>2000	...
(3) Se toning, unwashed	7.0	63	195	...
washed	7.0	27	76	420
unwashed, incubated.	7.0	700	...	...
washed, incubated.	7.0	360	1250	...
(4) Control, no toning.	7.0	2	6	14

tion period for untreated samples is not greatly affected. However, after a few samples have been tested in the solution, the induction period decreases. This decrease is apparently caused by silver ions in the solution. When a few drops of 1 *M* silver nitrate solution are added to 40 ml of basic hydrogen peroxide, there is no difference in induction period between samples which contain silver and those which do not. This instability of the basic hydrogen peroxide solution makes accurate work above pH 10 difficult.

The data referred to in the preceding paragraphs were obtained with Emulsion *B*. Emulsions *B* and *C* gave similar results. The induction period of Emulsion *A* is about seven times longer than those of the other emulsions. Treatment of Emulsion *B* with a 4 percent solution of formaldehyde for one hour increases the induction period for 16.5 percent peroxide from 7 to 17 seconds, even after water-washing of the pretreated sample. Thus, it seems probable that the induction period is increased by hardening the gelatin.

The induction period decreases with decreasing temperature with all the samples tested. In Figure two, the logarithms of the reciprocal induction periods for Emulsion *A* are plotted against the reciprocal of the absolute temperature. The data follow the Arrhenius equation reasonably well, with an apparent activation energy of 12 kcal/mole. The energies measured with Emulsion *B* are between 11 and 15 kcal/mole. This energy is not affected by the pAg of the pretreatment solution; for example, the energy for Emulsion *B* bathed in 0.01 *M* potassium bromide solution is 13 kcal/mole, and the energy for the same emulsion bathed in 10^{-4} *M* silver nitrate solution is 13 kcal/mole. Selenium toning increases the energy to about 15 kcal/mole.

Following a suggestion by R. W. Henn, of these Laboratories, the effect of selenium toning was tested. The samples were immersed in a dilute toning solution.[16] The effect of this treatment is shown in Table II. In the incubation treatments, the samples were removed from the toning bath, adjusted to the desired pH by immersion

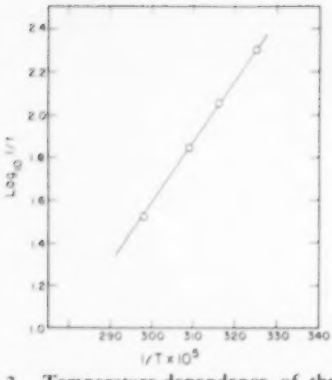


Figure 2. Temperature-dependence of the oxygen evolution induction period: "T" is the absolute temperature in degrees Kelvin; "t" is the induction period in seconds.

in a solution of the proper concentration, blotted dry with filter paper, and heated at a temperature of 40 C for 28 hours. In some cases, the samples were washed with distilled water at pH 6 for 5 minutes before drying.

Two conclusions may be drawn from these data. First, the induction periods of the unwashed selenium-toned samples do not follow the inverse-proportionality rule previously stated. Second, incubation of the samples at 40 C has a large effect on the induction period, particularly with the samples at pH 2.

Various surface coating treatments were tested. Thiourea was selected as a typical organic coating agent, and its effect was studied as a function of incubation and pH. In marked contrast to the selenium-toned sample, incubation has no effect on the induction period of thiourea-treated samples. The induction periods of water-washed and unwashed samples are summarized in Table III. These data indicate that the failure of the inverse-proportionality law is related to lack of washing.

The effects on the induction period of a number of thioureas were tested by immersing the sample in a 0.001 *M* solution for 30 minutes, followed by a 5-minute water-wash, and filter-paper drying. The results of these tests are summarized in Table IV. All of the

Table III

EFFECT OF THIOUREA PRETREATMENT ON THE INDUCTION PERIOD OF MACHINE-PROCESSED 5302 EMULSION AT 23 C

Sample Description	pH	Induction Period in Seconds in 33% H_2O_2	16.5% H_2O_2	8.25% H_2O_2
(1) Thiourea, 0.001 *M* 5-min wash	5.9	8	17	31
(2) Thiourea, 0.01 *M* unwashed	5.9	95	300	480
same, washed		19	42	92
(3) Thiourea, 0.01 *M* unwashed	3.0	21	62	110
same, washed		10	21	72
(4) Thiourea, 0.01 *M* unwashed	2.0	57	310	2000
same, washed		12	37	103
(5) Water control	5.9	2	6	15

Table IV

EFFECT OF VARIOUS THIOUREAS ON THE INDUCTION PERIOD OF MACHINE-PROCESSED 5302 EMULSION AT 23 C

Thioureas	pH	Induction Period in Seconds 16.5% H_2O_2
(1) Sym. di-*o*-tolyl 50% EtOH	6.0	36
(2) Sym. didecyl 75% EtOH		34
(3) Sym. *n*-dibutyl	6.3	26
(4) Asym. ethyl phenyl 50% EtOH	6.5	22
(5) Ethylene	6.1	20
(6) Sym. ethyl phenyl 50% EtOH	6.1	20
(7) Diethyl	6.1	17
(8) Allyl	6.0	17
(9) Tetramethyl	6.1	17
(10) Dimethyl	6.1	17
(11) Sym. diphenyl 50% EtOH	6.3	17
(12) Phenyl	6.4	16
(13) Sym. ethanol phenyl	6.1	13
(14) Methyl	6.1	11
(15) Water control	6.1	6
(16) 50% EtOH Control	6.6	17

measurements were made at 23 C, and the inverse-proportionality law was followed within the limits of error of the experiments. Therefore, only the induction periods of the 16.5 percent peroxide solution have been recorded. The thioureas are listed in the order of their effectiveness. As with thiourea itself, washing the emulsion after treatment decreases the induction period. Thiourea-treated samples dissolve when immersed in hydrogen peroxide, but this solution occurs after the start of gas evolution and does not interfere with the measurements.

The effects of a number of other sulfur-containing compounds are summarized in Table V. Again, inverse proportionality is followed and only the 16.5 percent peroxide values have been recorded. In general, nitrogen-containing compounds are not very effective in increasing the induction period. The results of these tests are summarized in Table VI. The catalytic effect of potassium cyanide may be due to an increase in the active silver surface, caused by the solution of adsorbed silver salts.

The effects of oxalic, malonic, glutaric, and adipic acids on the induction periods were measured. The results agree with the pH variation data just presented. No special effects of the organic portion of the molecule were observed.

Discussion

An explanation of the reaction inhibition can be established on the basis of the present work and from previous studies of the metal-catalyzed decomposition of hydrogen peroxide. The reactions suggested by Weiss and Abel are consistent with most of the facts. Reactions (1) and (5) oxidize silver to silver ion, causing loss of silver. Reactions (2), (3), and (6), are chain-propagating reactions. Reactions (4), and (7) are chain-terminating reactions which cause the evolution of oxygen observed in the peroxide decomposition.

The silver-catalyzed decomposition is a surface reaction and hence its rate will depend on surface conditions. The reaction proceeds without a significant induction period when the silver surface is freshly formed. Gelatin, which is adsorbed by silver, causes an induction period. Other compounds, such as thioureas, extend the induction period. The increase in the period with decreasing density of the silver deposit indicates that some portions of the silver are more susceptible to peroxide attack than others. Increasing the silver concentration increases the probability that an exposed silver site will be available. The hydroxyl radicals formed by reaction (1) will attack the adjacent gelatin, increasing the amount of exposed silver surface. When the gelatin and other protective substances have been oxidized, the reaction will proceed by reactions (2) to (7) and oxygen evolution will be observed. The induction period is inversely proportional to the peroxide concentration in most cases, indicating that reaction (1) is rate-determining.

The protective action of low pH is probably due to the suppression of hydrogen peroxide and radical ionization, inhibiting reactions (2), (4), and (6). As noted by

Table V

EFFECT OF VARIOUS SULFUR-CONTAINING COMPOUNDS ON THE INDUCTION PERIOD OF MACHINE-PROCESSED 5302 EMULSION AT 23 C

Sample Description	pH	Induction Period in Seconds 16.5% H_2O_2
(1) 2-Thiobarbituric acid unwashed 0.001 *M*	3.5	40
(2) Same, washed		20
(3) *o*-Benzoic sulfimide 0.001 *M* unwashed	3.7	20
(4) Same, washed		17
(5) 1-Benzoyl-2-thiohydantoin 0.001 *M* unwashed	3.6	19
(6) Same, washed		16
(7) Guanidine thiocyanate 0.01 *M*	5.7	16
(8) Cysteine, washed, 0.001 *M*	8.0	10
(9) Thiophenylacetamide 0.01 *M* washed	11.5	10
(10) 2-Thiouracil 50% EtOH 0.001 *M*	6.5	5
(11) Sodium sulfide, 0.002 *M*	11.1	7
(12) Water control	6	6

Table VI

EFFECT OF NITROGEN-CONTAINING COMPOUNDS ON THE INDUCTION PERIOD OF MACHINE-PROCESSED 5302 EMULSION AT 23 C

Sample Description	pH	Induction Period in Seconds 16.5% H_2O_2
(1) *p*-Methyl aminophenol H_2SO_4, 0.01 *M*	4	16
(2) *p*-Methyl aminophenol H_2SO_4, 0.01 *M*	5.3	13
(3) *p*-Methyl aminophenol H_2SO_4, 0.01 *M*	7.5	13
(4) Pyridine, 0.01 *M*		12
(5) Pyridine, 0.001 *M*		12
(6) *p*-Phenylenediamine, 0.01 *M*	7.7	11
(7) a,a'-Dipyridyl, 0.001 *M*		11
(8) Diethanolamine, 0.001 *M*		10
(9) Diethanolamine, 0.01 *M*		9
(10) Dimethylamine, 0.01 *M*		10
(11) Potassium cyanide, 0.001 *M*	9.8	2
(12) Potassium cyanide, 10^{-3} *M*		6
(13) Potassium cyanide, 10^{-4} *M*		7
(14) Water control	6.0	6

Abel,[5] reaction (3) does not appear to be important in this decomposition. If both reactions (3) and (7) occurred, oxygen evolution would be observed at low pH after the gelatin had been destroyed. Actual observation shows that the silver of the acid-treated samples is attacked markedly before flotation occurs, and action occurs in areas where no oxygen bubbles accumulate, as well as where they do accumulate. Thus, the OH radicals produced by reaction (1) do not form oxygen by reactions (3) and (7). Because of the suppression of the chain reaction, the flotation time is not a reliable indication of the destruction of the protective substances at low pH.

When the pH of the hydrogen peroxide solution is increased, the induction period no longer depends on the density of silver present in the samples if silver ions are present in the solution. In this case, the rate-determining processes are probably reactions (4) and (6), and perhaps reaction (2). The gelatin-coated sample presumably acts as a nucleus for evolution of oxygen.

Hardening the emulsion gelatin will decrease the rate of reaction of gelatin with radicals, and the silver particles will remain covered for a longer period. Treatment of the emulsion with solvents for silver compounds will clean the silver and increase its reactivity. The exceptionally high protective action of selenium toning can be explained by the conversion of silver to silver selenide. The latter presents a much less effective catalytic surface for the decomposition of hydrogen peroxide and will decrease the rate of reaction (1). Silver sulfide is likewise less active than silver. The activation energy of decomposition is somewhat higher on the silver selenide surface, and this difference is large enough to account for the large difference in the induction period. It is also possible that the surface is not completely covered by the silver selenide and that the decomposition occurs at cracks in the layer. The increase in induction period with incubation supports this hypothesis. During incubation, the silver selenide can diffuse over the silver surface and form a more compact layer.

Thioureas and other sulfur compounds can inhibit evolution of oxygen by reacting with hydrogen peroxide in the gelatin, as described by Kitamura.[18,19,20,21] This inhibition can be removed by washing the samples in water after treatment. In addition, adsorbed layers of these compounds can react with hydroxyl radicals or hydrogen peroxide at the silver surface, preventing evolution of oxygen. The present results do not indicate which of these reactions predominates. The results in Table VI show that inhibition by reaction or adsorption to the silver occurs with nitrogen-containing organic compounds. However, these substances do not appear to be so effective as the thioureas or other sulfur-containing compounds.

Conclusions

The reaction of hydrogen peroxide with finely divided silver imbedded in gelatin can be inhibited by coating the silver with various organic and inorganic compounds. A simple method has been devised to measure the extent of this inhibition. The results of the experiments can be explained by the mechanism suggested by Weiss and Abel. Electrons are transferred from the silver metal to the hydrogen peroxide. The OH radicals produced by this transfer then react with gelatin or with other compounds in the sample. When these compounds have been oxidized, the radicals propagate a chain and liberate molecular oxygen. The apparent activation energy of the induction-period reaction is about 12 kcal/mole for uncoated samples and about 15 kcal/mole for selenium-toned samples.

Selenium toning is the most effective treatment in protecting the silver from attack. Sulfur-containing organic compounds like thioureas also inhibit the reaction. The inhibitors can act in two ways. They can prevent the transfer of an electron from the silver, or they can react with hydrogen peroxide or radicals. Silver ions and cyanide ions accelerate the reaction.

Bibliography

1. M. Andresen, Phot. Korr., Vol. 36, p. 260 (1899).
2. H. Lüppo-Cramer, Phot. Korr., Vol. 48, p. 466 (1911).
3. E. J. Wall, "The History of Three-Color Photography," American Photographic Publishing Co., Boston, Mass., p. 356 (1925).
4. J. M. Centa, PSA Journal, Vol. 11, p. 22 (1945); Vol. 11, p. 77 (1945).
5. G. Bredig and R. M. von Berneck, Z. physik. Chem., Vol. 31, p. 258 (1899).
6. S. Berkman, J. C. Morrell, G. Egloff, "Catalysis, Inorganic and Organic," Reinhold Publishing Corp., New York, N. Y. (1940).
7. J. H. Baxendale, "Advances in Catalysis and Related Subjects," Volume IV, Academic Press, Inc., New York, N. Y., p. 31 (1952).
8. E. Abel, Monatsh. f. Chem., Vol. 83, p. 422 (1952).
9. J. Weiss, "Advances in Catalysis and Related Subjects," Volume IV, Academic Press, Inc., New York, N. Y., p. 343 (1952).
10. J. Weiss, Trans. Faraday Soc., Vol. 31, p. 1547 (1935).
11. G. Bredig, Z. Elektrochem., Vol. 32, p. 581 (1906); G. Bredig and K. Ikeda, Z. physik. Chem., Vol. 37, p. 1 (1901).
12. D. McIntosh, J. Phys. Chem., Vol. 6, p. 16 (1906).
13. E. Wiegel, Z. physik. Chem., Vol. 143A, p. 81 (1929).
14. E. Abel, Monatsh. f. Chem., Vol. 79, p. 457 (1948).
15. F. Haber and J. Weiss, Proc. Roy. Soc. (London), Vol. A147, p. 332 (1934).
16. R. W. Henn, private communication.
17. L. J. Fortmiller, T. H. James, R. F. Quirk, and W. Vanselow, J. Opt. Soc. Amer., Vol. 40, p. 489 (1950).
18. R. Kitamura, J. Pharm. Soc. Japan, Vol. 58, p. 818 (1938).
19. R. Kitamura and S. Suzuki, J. Pharm. Soc. Japan, Vol. 57, p. 659 (1937).
20. R. Kitamura, J. Pharm. Soc. Japan, Vol. 58, p. 804 (1938).
21. R. Kitamura, J. Pharm. Soc. Japan, Vol. 58, pp. 809, 825 (1938).

THE RATE OF SOLUTION OF SILVER HALIDE GRAINS IN A DEVELOPER*

T. H. James and W. Vanselow

ABSTRACT

A method has been devised for determining the rate of solution of silver halide grains in various solvents. The method depends upon the fact that the grains, as normally prepared, can be mixed with a Carey-Lea silver sol and coated, without becoming fogged in the process. The silver sol particles form excellent nuclei for physical development. If development conditions are chosen so that the rate of reduction of silver ions at the nuclei is rapid compared with the rate of accumulation of silver, the latter is determined primarily by the rate of solution of the silver halide.

The influence of bromide ion up to a concentration of 200 grams of potassium bromide per liter on the rate of solution of grains of a motion-picture positive emulsion was determined. The rate of solution passes through a minimum at a potassium bromide concentration of about 0.2 g/l., then increases with increasing concentration. The shape of the rate-concentration curve resembles that of the solubility curve, but there is no simple quantitative relation between the two. Thiocyanate markedly increases the rate. The temperature-dependence follows the Arrhenius relation, and the activation energies vary from 15 to 20 kcal/mole, depending on the solvent.

Ammonia is considerably more effective than bromide but less effective than thiocyanate in promoting solution of the grains. α-Picolinium-β-phenylethyl ion is somewhat less effective than ammonia or thiocyanate at equal molar concentrations. Sulfite is much less effective.

Rate determinations were made on unsensitized pure AgBr emulsion and on a 50 percent AgBr-AgCl emulsion of substantially the same grain size and coated with the same amount of Carey-Lea silver sol. The rate of solution of the chlorobromide emulsion was not much greater than that of the pure bromide. The rate of solution in an unhardened pure AgBr emulsion was about double that in a hardened emulsion.

The data on rate of solution are discussed in reference to the mechanism of photographic development. It is concluded that solvent action does not play a major part in the mechanism of propagation of development throughout a grain which has already started to develop in a surface-type developer or in a high-activity developer containing sodium sulfite as solvent. A significant amount of physical development occurs in an active Metol-hydroquinone developer containing thiosulfate.

It is customary in discussions of the mechanism of photographic development to distinguish two types, one termed "physical," the other "chemical" development. The precise meaning of these terms is not always stated, and sometimes the terms are used rather loosely. A clear distinction can be made on the basis of procedure between "postfixation physical" development and "direct" development. In the former, the silver halide is dissolved out before development, and the developing solution contains a soluble silver salt which supplies the silver for the development. In the latter, the exposed photographic material is introduced into a developer which initially contains no silver salt, and the silver for development is derived solely from the silver halide. This latter type is often termed "chemical development," although it is recognized that two processes may be involved. The silver halide may be reduced by an essentially direct attack of the developer on the solid. Some writers reserve the term "chemical development" for this mechanism. It is also possible that at least some silver halide dissolves in the developer, and the silver ions from the solution are reduced at the latent-image centers by the same mechanism as that which operates in postfixation physical development. This process could be called physical development. It has been stated that in ordinary development practice, both types of development occur, and that the relative importance of each is determined by the existing conditions.[1,2] The solvent action of sulfite, which is normally present, and that of thiocyanate, which is sometimes present in conventional developers, are believed to promote physical development.

Several studies have been made of the equilibrium solubility of silver halides in solutions which contain sulfite, bromide, carbonate, and thiocyanate ions. Data are not available on the rate of solution of silver halide grains in these solutions, and the rate of solution probably is more important than equilibrium solubility in determining the extent to which physical development occurs. The present work was undertaken to obtain information on the relative rates of solution of typical emulsion grains in various solvents which might be present in a developer.

Experimental Method and Material

The method used to measure the rate of solution of the silver halide grains depends upon the fact that the grains, as normally prepared, can be mixed with a Carey-Lea silver sol and coated, without becoming fogged in the process. The silver sol particles form excellent nuclei for physical development, and solution of the silver halide in the developer can supply the silver ions for this purpose. If development conditions are chosen so that the rate of reduction of silver ions at the nuclei is rapid compared with the rate of accumulation of silver, then the latter is determined by the rate at which the silver ions arrive at the nuclei. This rate could be determined either by the rate of solution of the silver halide or the rate of diffusion of silver ions or ion complexes through the gelatin. If the rate of solution is rapid compared with the rate of diffusion, the measured rate of accumulation of silver at the nuclei should be related simply to the

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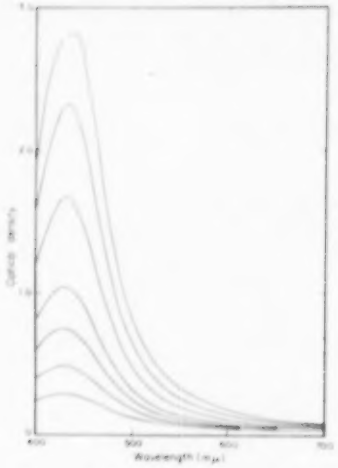


Fig. 1. Spectral absorption curves for development of unexposed coating, *A*, in the M-AA-3 developer containing 20 g of KBr/l. at 20.2 C. Development times: 0.5, 1.0, 1.5, 2.0, 2.75, 3.5, and 4.25 minutes.

solubility of the grains in the particular solvent. This is so because the rate of diffusion will be determined by the concentration gradient surrounding the nuclei, and the higher the concentration of silver ions in solution, the larger will be this gradient. The experimental data clearly show that diffusion is not rate-controlling when the solvent is sulfite ion. The evidence, in general, suggests that the rate of physical development measured under the conditions employed in most of the present work is determined by the rate of solution of the silver halide.

The photographic material used in the major part of this work was a hardened, high-contrast, motion-picture positive-type emulsion to which Carey-Lea silver sol (CLS) had been added before coating. The size of these silver particles was in the range of 5 to 50 mμ. Two film coatings were prepared with a five-fold difference in the amount of Carey-Lea silver added. Coating *A* contained, by analysis, 0.099 mg of silver per 100 sq cm, and Coating *B* contained 0.481 mg of silver per 100 sq cm. The total amount of halide silver in the coatings was 35.2 mg per 100 sq cm.

Three other experimental coatings were prepared by W. G. Lowe, of these Laboratories: *C* was an unsensitized pure silver bromide emulsion coated with 2.03 g of CLS per mole of silver bromide; *D* was a coating of the same silver bromide emulsion with 0.813 g of CLS per mole of silver bromide; *E* was an unsensitized 50-50 AgCl-AgBr emulsion coated with 2.03 g of CLS per mole of silver halide. These emulsions were hardened and coated similarly to the motion-picture positive-type emulsion. The average grain size of Emulsions *C* and *E* was about equal, and somewhat smaller than that of Emulsion *B*.

All tests were carried out on unexposed materials. The developers were prepared and used in a nitrogen developing apparatus.[2] Agitation was supplied by irregular bursts of nitrogen. The strips of film used were 17.5 mm by 15 cm, and were held at each end secured by rubber bands to the inner tube of the developing apparatus. The developed strips were fixed, washed, and dried as usual.

Total density curves were obtained on each sample over the wavelength range of 400 to 700 mμ. A series of curves obtained by development of Emulsion *A* in Metol-*d*-araboascorbic acid developer of pH 10.3 (M-AA-3, see below) containing 20 g. of KBr/l. is shown in Figure one. The curves show a sharp maximum at a wavelength of about 430 mμ, and the position of the maximum remains nearly constant to a density of over 2.0. The absorption follows Beer's law with fair accuracy within this range. Electron-micrographs, however, show that the particle size increases with increasing density.

The density formed by the same developer acting on a control emulsion which contained no colloidal silver is essentially neutral. The densities developed on this control emulsion usually are only slightly lower than the density read at 700 mμ on the emulsions containing the CLS. Hence, the densities read at 700 mμ on the latter film can be used as a correction, to a first approximation, for fog silver produced by direct reduction of the silver halide grains. In most experiments, the correction involved was negligible.

Direct silver determinations were obtained on strips of film developed for various times in several different developers, and the mass of silver was correlated with the density determinations. The developers chosen produced quite low densities at 700 mμ for the times of development used, and total density at the absorption maximum, or at 480 mμ, was plotted against the mass of silver per unit area. Representative results for various emulsion coatings and developers are shown in Figure two. The silver-density relation is linear over the density range used in the rate calculations.

Experimental Results

Preliminary experiments were carried out to determine the amount of physical development which would occur in a typical Metol-*d*-araboascorbic acid surface de-

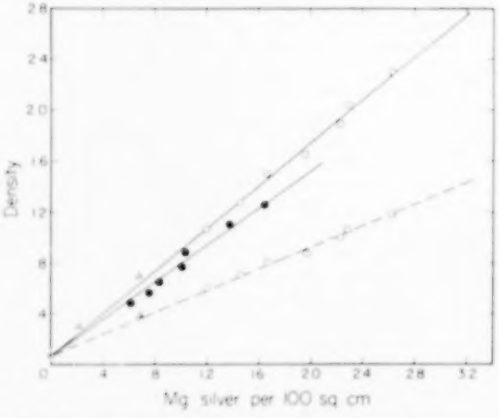


Fig. 2. Silver-density relation for pure AgBr emulsion: ○○, Coating *C*; ●●, Coating *D*; △△, undeveloped emulsion; — density at absorption maximum: – – –, density at 480 mμ.

veloper, M-AA-1,[4] which contained 1 g. of KBr/l. but no quaternary salt. The control coating which contained no silver sol had very little fog silver, even after 45 minutes' development. On the other hand, in Coating *B*, 5 percent of the total silver halide present had physically developed at the silver nuclei in 26 minutes. The same amount of silver halide physically developed in a typical motion-picture negative developer in about 4 minutes. This developer was composed of 1.5 g of Metol, 75 g of sodium sulfite, 1.3 g of hydroquinone, 4.5 g of borax, and 0.4 g of KBr/l.

The Metol-*d*-araboascorbic acid combination was chosen as a standard developer for the present work, since it could be used in the absence of sulfite without complications from staining oxidation products. The pH of the M-AA-1 composition, 9.5, proved too low, however, as the rate of reduction of silver ions at this pH was not high enough in the presence of some solvents. At pH 10.3, the rate of development in the presence of any of the solvents used was independent of the concentration of Metol over the tested range of 0.84 to 9.6 g/l. and further increase in pH did not increase the rate. This is illustrated in Figure three for a developer containing 1 g

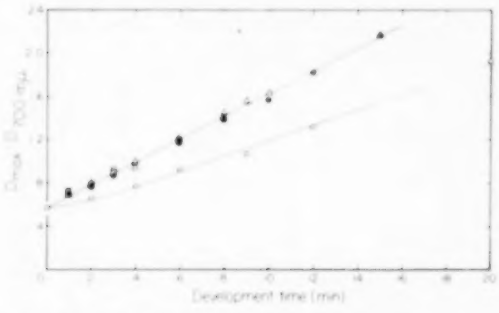


Fig. 3. Development of Coating *B* at 20.2 C.

	Metol	*d*-araboascorbic acid	KBr	pH
○○	2.5	10.0	1.0	9.5
▲▲	0.84	10.0	1.0	10.3
●●	9.6	10.0	1.0	10.2
△△	2.5	10.0	1.0	11.6
□□	Amidol 2.8	...	1.0	10.2

of KBr/l. As a further check, a sulfite-free Amidol developer containing 2.8 g of developing agent at pH 10.2 was tried, and found to develop at the same rate. The Amidol developer is useful only for short times of development, because it rapidly attacks the silver halide grains and reduces them directly. The rate of physical development by this developer before direct fogging becomes serious is the same as the rate of physical development by the Metol-*d*-araboascorbic acid solution.

The developer composition used in most of the subsequent experiments was as follows:

M-AA-3

Metol	2.5 g
d-Araboascorbic acid	10.0 g
Sodium carbonate monohydrate	55.6 g
Water to 1 liter, pH 10.3 at 20 C	

The various emulsions were tested in the M-AA-3 developer to which 1 g of KBr/l. had been added. Table I

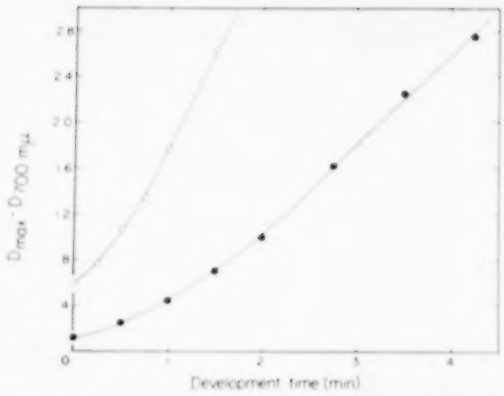


Fig. 4. Dependence of rate of development on concentration of Carey-Lea silver. ●●, Coating *A*; ○○, Coating *B*; Temp. 20.2 C. M-AA-3 developer + 20 g of KBr/l.

gives the rate of physical development in terms of the slopes of the linear portion of the density-time curves. A similar test was carried out in the absence of added bromide in the developer, and the results are also given in Table I. The developer for the latter tests was used at pH 9.5 to decrease direct fog formation. However, a test made at pH 10.3 gave essentially the same rate of physical development. In the absence of bromide, therefore, the rate of development became independent of pH at a pH as low as 9.5. The rate measured for the chlorobromide emulsion was somewhat higher than that for the pure bromide, but the difference was much less than the difference in solubility. The rate of physical development in Coating *B* was not much lower than that in the pure bromide.

The rate of physical development in an unhardened emulsion was higher than in a hardened layer. This is illustrated by the results obtained with the pure silver bromide emulsion, *C*. The maximum rate of physical development by M-AA-3 with 1.0 g of KBr/l. was 0.292 for a sample coated without hardener. The rate was 0.135 for a sample coated with hardener.

The rate of physical development of Coatings *A* and *B* was measured at various potassium bromide concentrations. The density-time-of-development curves for bromide concentrations of 1 g/l. or less were linear over most of the measured course, and showed little or no induction period. An induction period appeared at higher bromide concentrations, and became particularly marked

Table I

DEPENDENCE OF RATE OF DEVELOPMENT ON THE EMULSION AND DEVELOPER COMPOSITION AT 19.8 C

Coating	Ag Halide as:	Slope Rate No KBr	In Presence of 1.0 g/l.	Developer pH
B	Br, I	0.118	...	9.5
B	Br, I	0.120	0.102	10.3
C	Br	0.168	...	9.5
C	Br	...	0.133	10.3
E	Cl, Br	0.220	...	9.5
E	Cl, Br	...	0.160	10.3

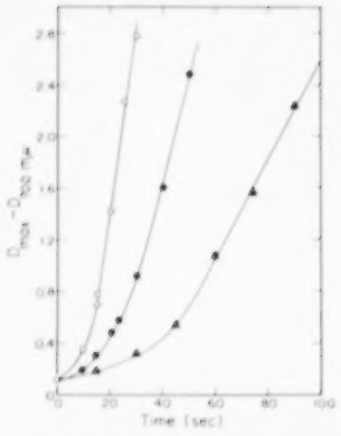


Fig. 5. Density-time-of-development curves for M-AA-3 developer + 200 g of KBr/l. Coating *A*. ○○, 20.5 C; ●●, 14.0 C; ▲▲, 8.4 C.

at 200 g of KBr/l. Figure three shows the curves obtained for 1 g of KBr (Coating *B*). Figure four shows the curves obtained for 20 g of KBr and the two concentrations of Carey-Lea silver sol. Figure five shows the curves obtained for 200 g of KBr and three different temperatures. Table II gives numerical data for the densities at the absorption maximum and at 700 mμ for different times of development and different bromide concentrations.

The rate of physical development is measured in terms of the reciprocal of the time required to obtain a given density, and in terms of the maximum slope of the density-time curve. The reciprocal time rates are measured at a $D(\max) - D(700\ m\mu)$ value of 1.00 for Coating *B* and of 0.40 for Coating *A*. The density increment above that of the original Carey-Lea silver is thus about 0.4 for the first emulsion, 0.3 for the second. The slope rates are given in terms of density units per minute and of percent silver halide converted to silver per minute.

Table III gives the rate data for Coating *B* and various bromide concentrations. The rate drops, at first, with increasing bromide concentrations, passes through a minimum, and then increases. This is shown graphically in Figure six, where rate is plotted against the square root of the bromide concentration. The solubility of silver bromide at 25 C, as determined by Moyse, Ballard, and Sheppard,[5] is included for comparison.* The general form of the curves is similar, but the quantitative relations are different. Solubility data at 20 C are not available, but extrapolation of the temperature-dependence data given by Moyse, Ballard, and Sheppard[5] indicates that the difference in temperature cannot account for the difference between the rate and solubility curves. The amount of iodide present in the emulsion grains is not

* The method of determining the solubility of silver bromide was, in principle, that used by S. Popoff and E. W. Newman, (J. Phys. Chem., Vol. 34, pp. 1853-60 [1930]) to investigate the solubility of silver chloride in dilute chloride solution. Carefully measured amounts of a silver solution and a bromide solution were mixed until a just-visible permanent turbidity resulted. Because the accuracy of the method depends mainly on the procedure used to detect a permanent turbidity, a special tyndallmeter was constructed using quartz tubes remarkably free from imperfections. Readings were made in the tyndallmeter at various times until equilibrium was reached.

Table II

DENSITY DATA FOR DEVELOPMENT OF EMULSION *B* IN THE M-AA-3 DEVELOPER, pH 10.3, 20.2 C

Time (min)	No KBr		0.2 g KBr		5.0 g KBr		20.0 g KBr	
	D_m	D_{700}	D_m	D_{700}	D_m	D_{700}	D_m	D_{700}
0.5	0.69	0.06	...	...	...	...	1.12	0.05
1.0	.77	.07	0.66	0.06	0.86	0.05	1.83	.06
1.5	.83	.08	...	...	...	...	2.70	.07
2.0	.90	.09	.74	.06	1.17	.05	...	.09
3.0	1.06	.12	.82	.06	1.49	.06	...	...
4.0	1.21	.16	.86	.07	1.86	.07	...	...
6.0	...	...	1.02	.10	2.62	.08	...	...
8.0	...	...	1.20	.14	...	...	...	...
10.0	...	...	1.42	.20	...	...	...	...
12.0	...	...	1.60	.25	...	...	...	...

sufficient to cause a significant change in the solubility relation. Moreover, slope-rate data given in Table I show that the addition of 1 g of KBr to the developer causes nearly the same decrease in rate for the pure bromide emulsion as for the bromoiodide.

The temperature-dependence of physical development was determined at various bromide-ion concentrations for Coatings *A* and *B*. The data are listed in Table IV. The rate follows the Arrhenius equation, as shown by the straight lines obtained in a plot of log rate against

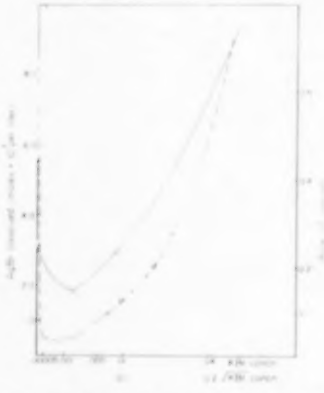


Fig. 6. Comparison of rate of solution with solubility.
———, rate of solution in Coating *B* at 20 C;
– – –, solubility of AgBr at 25 C.

the reciprocal of the absolute temperature. The slope of the straight line, and hence the calculated activation energy, are essentially independent of the method used to express the rate of development. The activation energy also is the same for the two concentrations of Carey-Lea silver used in the two coatings. Activation energies calculated for the various conditions are listed in Table V for 0, 1, 20, and 200 g of KBr/l. The activation energy is increased by the addition of 1 g of KBr, but decreased by the higher concentrations.

Sodium sulfite is normally present in commercial photographic developers in concentrations up to 100 g/l. The solubility of silver bromide in water is greatly increased by the presence of sulfite, even when excess bromide ion also is present. Sulfite increases the rate of solution (physical development) of silver halide emulsion grains,

Table III

DEPENDENCE OF RATE ON BROMIDE CONCENTRATION
COATING *B*, 20.2–20.3 C

KBr (g/l.)	1/t (D = 1.0)	Slope (D/min)	Slope (%/min)
0	0.25	0.11	0.28
0.02	.19	.088	.22
.20	.14	.067	.17
1.0	.22	.091	.23
5.0	.61	.37	.94
10.2	1.25	.7	1.78
20.0	2.5	1.6	4.1
200.0	(13.2)	(14.9)	(38.0)

Table IV

TEMPERATURE-DEPENDENCE FOR VARIOUS KBr CONCENTRATIONS

°K Temp	1/t (min⁻¹)	Slope (D/min)	Slope (%/min)	KBr	Coating
282.7	0.10	0.053	0.14		*B*
293.1	.29	.144	.37		*B*
303.2	.85	.38	.97		*B*
283.6	.061	.030	.076	1.0	*B*
292.8	.185	.092	.24	1.0	*B*
293.4	.227	.10	.26	1.0	*B*
302.6	.588	.268	.68	1.0	*B*
283.4	.028			1.0	*A*
292.8	.089			1.0	*A*
303.5	.303			1.0	*A*
283.3	.87	.61	1.56	20.0	*B*
293.2	2.22	1.71	4.36	20.0	*B*
303.7	5.88	4.3	11.0	20.0	*B*
283.2	0.42	0.304	0.86	20.0	*A*
293.2	1.11	.82	2.33	20.0	*A*
303.7	3.23	2.2	6.2	20.0	*A*
281.4	1.67	2.5	7.1	200.0	*A*
287.5	3.16	4.8	13.6	200.0	*A*
293.3	5.45	8.5	24.1	200.0	*A*

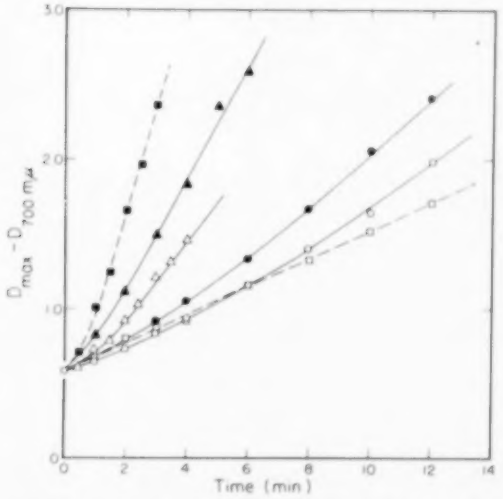


Figure 7. Effect of sulfite concentration on rate of physical development at 20.4 C. M-AA-3 + 1.0 g KBr/l. Coating *B*: □□, No sulfite; ○○, 1.3 g of sulfite; ●●, 6.67 g of sulfite; △△, 33.3 g of sulfite; ▲▲, 66.7 g of sulfite/l. ■■, 0.5 g of KCNS/l.

but the effect of sulfite on the rate of solution is relatively much less than its effect on solubility. The density-time curves for various sulfite concentrations in the presence of 1 g of KBr/l. are given in Figure seven. Rate data are listed in Table VI. These data show, for example, that the rate of solution is not even doubled by the addition of 6.67 g of sodium sulfite. This amount of sulfite increases the solubility by more than three orders of magnitude.

Activation energies were determined for the rate of solution of the grains of Coatings *A* and *B* in a solution containing 66.7 g of sodium sulfite and 0 or 1.0 g of KBr per liter. Satisfactory Arrhenius plots were obtained and the calculated activation energies are given in Table V. The calculated activation energy is substantially the same as that obtained in the absence of the sulfite.

The measured rate of physical development in the sulfite solution is somewhat greater in the absence of added potassium bromide. Figure eight shows a comparison of the density curves for no bromide and 1 g of KBr. The coating used, *B'*, is substantially a duplicate of *B*.

Thiosulfate, thiocyanate, and ammonia are much more effective than sulfite in increasing the rate of physical development. Data for various concentrations of these agents are listed in Table VI. All solutions contained 1 g of KBr/l. When the developer contains thiocyanate

Table V

ACTIVATION ENERGIES IN VARIOUS SOLVENTS

Coating	Rate as	KBr (g/l.)	Other Addenda (g/l.)	Activation Energy	Average
B	1/t (D = 0.75)	...	...	19.1	
B	1/t (D = 0.90)	...	...	18.0	
B	1/t (D = 1.00)	...	...	18.0	
B	Max. slope	...	...	17.5	
					18.2
B	1/t (D = 1.0)	1.0	...	20.5	
	Max. slope	1.0	...	19.6	
A	1/t (D = 0.4)	1.0	...	20.3	
	1/t (D = 0.7)	1.0	...	20.1	
					20.1
B	1/t (D = 1.0)	20.0	...	16.2	
	Max. slope	20.0	...	16.0	
A	1/t (D = 0.4)	20.0	...	16.9	
	Max. slope	20.0	...	16.6	
					16.4
A	1/t (D = 0.4)	200.0	...	16.4	
	Max. slope	200.0	...	16.4	
					16.4
B	1/t (D = 1.4)	1.0	1.0 KCNS	14.8	
	Max. slope	1.0	1.0 KCNS	15.2	
A	1/t (D = 0.4)	1.0	1.0 KCNS	15.5	
	Max. slope	1.0	1.0 KCNS	15.2	
					15.2
B	1/t (D = 1.0)	1.0	66.7 sulfite	20.3	
	Max. slope	1.0	66.7 sulfite	20.1	
A	1/t (D = 0.4)	1.0	66.7 sulfite	20.3	
	1/t (D = 1.0)	1.0	66.7 sulfite	19.8	
					20.1
*B'**	1/t (D = 1.0)	...	66.7 sulfite	17.3	
	Max. slope	...	66.7 sulfite	18.4	
					17.9

**B'* is a repeat coating of *B*.

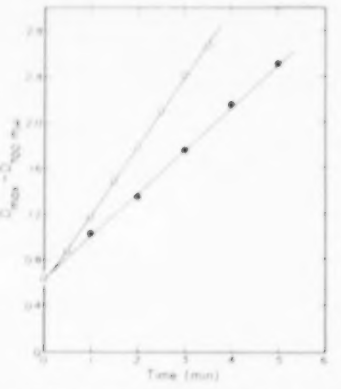


Figure 8. Effect of KBr on the rate of physical development in the presence of 66.7 g of sodium sulfite/l. Coating *B*; 20.0 C. ○○, no KBr; ●●, 1.0 g of KBr.

or ammonia, the curve representing density as a function of time is characterized by a relatively short "induction period" (region of increasing rate of increase of density) followed by a straight line. A linear relation between mass of silver and time holds well beyond the highest density which can be accurately measured. Figure nine shows the example of a developer which contained 5 g of KCNS/l. The linear relation holds until more than 50 percent of the silver halide has dissolved and been reduced to silver. Thiosulfate shows a much more pronounced induction period, and there is no evidence that a straight-line portion of the density-time curve has been reached up to a density of 3.0.

The quaternary salt used in the M-AA-2 standard surface-image developer,[4] α-picolinium-β-phenylethyl bromide, increases the rate of physical development almost as effectively as ammonia. Figure ten shows the effect of two concentrations of the quaternary salt. The amount of potassium bromide in each solution was adjusted so that the total amount of bromide ion was equivalent to 1 g of KBr/l. The quaternary salt also increases the rate in the presence of 66.7 g of sodium sulfite plus 1 g of KBr, but the relative increase is not so large as that obtained in the absence of sulfite.

Table VII lists the concentrations of the various solution promoters required to obtain a specified rate of physical development, and also the rate obtained at a fixed concentration of the solution promoter. Thiosulfate and thiocyanate are the most effective. Next in order are ammonia, the quaternary ion, and bromide. Sulfite is less effective than bromide by an order of magnitude.

Discussion

Experimental conditions have been selected so that the *specific* rate of reduction of silver ions by the developer is rapid compared with the measured rate of accumulation of silver. Hence, the chemical reaction is not rate-controlling. Two other possibilities are suggested for the rate-controlling process: (1) the solution of the silver halide, and (2) the diffusion of silver ions or silver-ion complexes to the silver nuclei. If (1) were rapid compared with (2), the concentration of silver ions or complex in the neighborhood of the silver halide grains would be determined largely by the equilibrium solubility of the halide. The rate of diffusion to the silver particles should increase with increasing concentration gradient, and hence with increasing concentration of silver ion or ion complex in the vicinity of the grain. The concentration at the silver particle surface is maintained at essentially zero by the rapid reaction at that surface. Experimentally, we find that agents which increase the solubility increase the rate, but there is no quantitative correlation between equilibrium solubility and the measured rate. The measured rate differs only slightly for pure silver bromide and for a 50–50 mixture of silver chloride and bromide. Additions of sulfite which increase the solubility 1000-fold increase the rate by only a few-fold, whereas additions of ammonia or thiocyanate which have much less effect on solubility have a greater effect on the measured rate. We conclude, therefore, that the measured rate is in the main

Table VI

DEPENDENCE OF RATE UPON CONCENTRATION OF SOLVENT

(All solutions contain 1 g KBr/liter)

Solvent	Concentration	1/t Rate	Max. Slope (D/min)	Slope (%/min)	Temp. °C	Coating
KCNS	0.50 g/l	1.00	0.63	1.6	20.3	*B*
KCNS	1.00 g/l	2.90	1.77	4.5	20.3	*B*
KCNS	2.00 g/l	5.55	3.7	9.4	20.3	*B*
KCNS	5.00 g/l	20.0	17.8	45.4	20.3	*B*
Sulfite	0.00 g/l	0.22	0.094	0.24	20.4	*B*
Sulfite	1.30 g/l	.21	.136	.35	20.4	*B*
Sulfite	6.67 g/l	.27	.18	.46	20.4	*B*
Sulfite	33.3 g/l	.43	.29	.74	20.4	*B*
Sulfite	66.7 g/l	.74	.40	1.02	20.0	*B*
Sulfite	66.7 g/l	.31	.20	0.57	20.0	*A*
Ammonia	0.01 *M*	1.18	0.72	1.84	19.8	*B*
Ammonia	.03 *M*	3.45	2.40	6.12	19.8	*B*
Ammonia	.01 *M*	0.67	0.48	1.36	19.8	*A*
Ammonia	.03 *M*	2.38	1.96	5.57	19.8	*A*
Ammonia	.10 *M*	14.3	11.6	32.9	20.0	*A*
Ammonia	.60 *M*	100	72	204.5	20.0	*A*
Thiosulfate	0.001 *M*	0.38	0.52	1.48	20.0	*A*
Thiosulfate	.010 *M*	1.54	(3.4)	(10)	20.3	*A*
Thiosulfate	.001 *M*	0.67	...	...	20.0	*B*
Thiosulfate	.010 *M*	2.33	(8)	(20)	20.3	*B*
Quaternary Salt	...	0.23	0.092	0.23	20.2	*B*
	.0017	.34	.146	.37	20.2	*B*
	.0084	.71	.35	.89	20.2	*B*

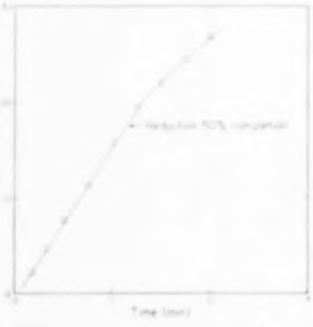


Figure 9. Development by M-AA-3 + 1.0 g of KBr + 5.0 g of KCNS/l. Coating *B*; 20.3 C.

Table VII

EFFECT OF VARIOUS SOLVENTS ON RATE OF SOLUTION OF GRAINS IN METOL-ASCORBIC ACID DEVELOPER AT pH 10.3 AND 20 C; COATING *B*; INITIAL KBr CONCENTRATION 1.0 g/l.

Solvent	Concentration of Solvent to Produce 1/t (D = 1.0)* Rate of 0.5	0.75	1/t Rate Increase Produced by Solvent Concentration of: 0.01 *M*	0.03 *M*
Thiosulfate	...	0.00125	2.1	...
KCNS	ca. 0.0025 *M*	ca. .0040 *M*	2.1	9.4
NH_3	.0032	.0057	0.96	3.2
α-Pic.**	.0047	.0092	.58	...
KBr	.024	.045	.11	0.35
Sulfite	.29	.56	.0	.03

* Rate in absence of added solvent: 0.22.
** α-Picolinium-β-phenylethyl ion.

determined by the rate of solution of the silver halide.

Diffusion effects, nonetheless, are of some importance in determining the quantitative rate. The maximum rate of solution would be achieved for a given solvent only if the silver ions were permanently removed as soon as they left the solid phase. Instead, they are permanently removed only when they reach the surface of a silver sol particle, and there is a finite probability that a given silver ion will return to the silver halide surface before it can reach the silver surface. This probability decreases as the number of silver nuclei per unit volume increases. Thus, we explain the observation that the measured rate is not independent of the concentration of silver particles. Actually, an increase of five-fold in the number of particles produces an increase of somewhat less than two-fold in the rate.

The mechanism of solution probably depends on the solvent. In the absence of excess bromide or other solvent, silver ion probably passes into solution as such or in a solvated state. The activation energy calculated from the temperature-dependence is about 18 kcal/mole. When a small amount of bromide ion is present in the solution, some of the excess bromide is adsorbed by the silver halide. This adsorbed bromide decreases the rate at which silver ions can leave the surface. The activation energy increases to at least 20 kcal/mole. When

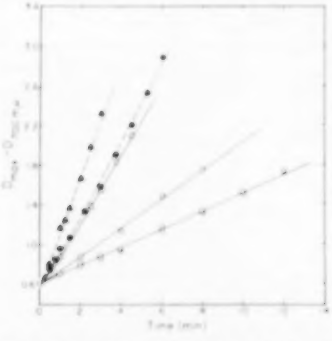


Figure 10. Effect of α-picolinium-β-phenylethyl ion on the rate of physical development. All solutions contain bromide equivalent to 1 g of KBr/l. Coating *B*; 20.2 C. ○○, no addition; □□, 0.47 g of α-picolinium bromide; △△, 2.33 g of α-picolinium bromide; ●●, 66.7 g of sodium sulfite; ▲▲, 66.7 g of sodium sulfite + 2.33 g of α-picolinium bromide.

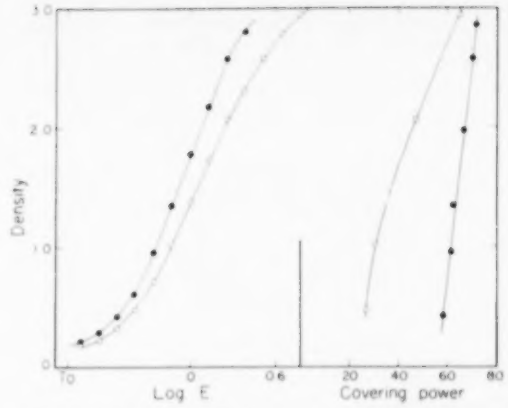


Figure 11. Characteristic curves and covering power for development of a motion-picture positive emulsion in a Metal-hydroquinone developer with and without addition of sodium thiosulfate. ●●, no thiosulfate; ○○, 5.0 g thiosulfate/l. 6 Minutes' development at 20 C.

larger amounts of bromide ion are present in the solution, the formation of the adsorption layer is followed by complex formation between the silver ions and bromide ions. It is now the negatively charged silver bromide complex ion which passes into solution rather than the positively charged free or solvated ion. The activation energy drops to about 16 kcal/mole. In this region, the rate of complex formation increases with increasing concentration of bromide ions, and the rate of solution likewise increases.

Sulfite, thiocyanate, thiosulfate, and ammonia likewise appear to dissolve the silver halide by complex formation in a surface reaction. Surface conditions can exert an important influence on the rate of this reaction. Sulfite forms a complex with silver ions of the following composition:

$$Ag(SO_3)_2^{---},$$

and ammonia forms a positively charged complex:

$$Ag(NH_3)_2^{+}.$$

The silver ion is more tightly held in the former than in the latter, but the rate of solution in sulfite is much slower. It may be assumed that at least one sulfite ion or ammonia molecule must be adsorbed per silver ion at the silver halide surface before complex formation can begin. Adsorption of the sulfite ion is discouraged by the fact that a doubly charged negative ion must be adsorbed by a negatively charged surface. There is no such impediment to the adsorption of the ammonia. Moreover, once the sulfite ion is adsorbed, the surface charge, if anything, will become more negative, thus impeding the approach of a second sulfite ion necessary for complex formation.

A similar "charge effect" will exist for the bromide ion and thiocyanate ion, but it will be of much less consequence. These ions are singly charged rather than doubly charged. The original negative charge on the silver halide surface is acquired from adsorption of bromide ion, and the only important charge effect will ap-

pear for the approach of the second halide or the thiocyanate ion necessary for complex formation. Experiments on the influence of charge on the rate of photographic development have shown that the relative influence of charge on rate is smaller by at least an order of magnitude for a singly charged ion than for a doubly charged ion.

On an equal molar basis, the rate of solution in thiosulfate is considerably greater than that in sulfite. Chromatographic experiments[11] have shown that the thiosulfate ion is much more strongly adsorbed by silver bromide than is the sulfite ion, and this strong adsorption should greatly favor the thiosulfate in the first stage of the solution process according to the mechanism suggested.

The present data lead to some conclusions as to the possible participation of solvent effects in normal photographic development. It is seen that silver bromide does go into solution even in the best surface developers. It is quite possible, therefore, that such developers may, in time, reach latent-image centers situated below the grain surface. However, the rate of solution is quite low in a developer which contains from 0 to 1 g of KBr/l. and no other solvent. The rate at 20 C is such that only 0.23 percent of the silver halide in the motion-picture positive emulsion would dissolve in 1 minute. On the other hand, 38 percent would dissolve in a solution which contained 200 g/l. These figures, of course, apply strictly only to the present experimental conditions. The quantitative values probably are different when the silver surface for physical development is supplied by active chemical development taking place in the vicinity of the dissolving surface, but a relative comparison based on the present figures should be valid.

In view of the rapid solvent action of bromide ion at high concentration, on silver bromide, we may inquire whether once a grain has started to develop, it does not continue to do so by way of a physical development mechanism. If the initial stage of development is rapid, a relatively high local concentration of bromide ions may form in the immediate vicinity of the development center. This process may take place to some extent, but the measured activation energies do not favor it as the dominant process. The activation energy of solution is about 16 kcal/mole both in the presence of 20 g and 200 g/l. The activation energy for continuation of development of a grain which has already started to develop is not higher than 10 kcal/mole in the Metol-*d*-araboascorbic acid surface developer or in a similar developer to which sulfite has been added.[5] Similarly, it does not appear that sulfite promotes a shift to physical development in the high-activity developers, since sulfite does not significantly change the activation energy of solution of the silver halide. The solvent action of the sulfite probably is of more importance in the very early stages of development of a grain than in the later stages.

We cannot draw definite conclusions from the data at hand as to the rôle of sulfite in the slow-acting fine-grain developers. Other work[7,8] has shown, however, that when the rate of development is low enough, sulfite can cause a transition from chemical to physical development. This transition is accompanied by a decrease in the net rate of development, and probably depends on an action of the solvent which isolates the latent-image centers from the silver halide and hence stops chemical development.[9] There would be little chance for such a transition to occur if the initial rate of development were high, as it is in the very active developer.

The rates of solution of silver halide in 0.5 percent KCNS, 0.1 *M* ammonia, or 0.01 *M* sodium thiosulfate are great enough to be of considerable significance even in rapid development. The rates are 45, 33, and 22 percent of the total silver halide dissolved per minute. The developers for internal image generally contain at least 0.01 *M* thiosulfate, and physical development may play an important part in the total development in such solutions. Activation energies are not available for comparison. It is significant, however, that the specific rate of reduction of silver ions at a silver surface by a rapid developer, such as Metol-*d*-araboascorbic acid, Metol-hydroquinone, or even pure Metol developer of pH 10 or above, is higher than the rate of solution. When such a developer contains a rapid-acting solvent, such as thiosulfate, silver from a grain which does not contain latent-image nuclei may physically develop onto the silver of an adjacent developed grain and cause a significant increase in the amount of silver in the developed grain. Stevens has suggested[12] that silver might be deposited by physical development on a chemically developed grain without even producing an increase in the over-all size of that grain, since the physically developed silver may simply fill in the spaces which exist in the original porous structure. Even if the size of the grain increased, density would not increase proportionally to the increase in the amount of silver.

Figure eleven illustrates the change in covering power observed in one experiment. The left half of this figure shows the characteristic curves obtained by developing Eastman Release Positive Film, Type 1301, for 6 minutes at 20 C in an active developer composed of 3 g of Metol, 45 g of sodium sulfite, 12 g of hydroquinone, 55.7 g of desiccated sodium carbonate, and 2 g of potassium bromide with and without the addition of 5 g of sodium thiosulfate per liter. The thiosulfate, which converts this solution into Stevens's internal developer,[10] causes some loss in density. It is quite probable that the thiosulfate has destroyed the developability of some grains by nucleus isolation.[8] As shown in the right half of the figure, the thiosulfate also causes a marked decrease in covering power in the toe region. Actually, more silver is developed in the toe region in the presence than in the absence of the thiosulfate, but the change in covering power is so large that a net loss in density is observed. In the shoulder region of the characteristic curve, where most of the grains contain latent-image nuclei and start to develop normally, there is much less transfer of silver from one grain to another, and the covering power shows little dependence on the presence of thiosulfate.

Bibliography

1. T. H. James and G. C. Higgins, "Fundamentals of Photographic Theory," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 82.
2. C. E. K. Mees, "The Theory of the Photographic Process," Revised edition, The Macmillan Co., New York, N. Y., 1954, p. 504.
3. T. H. James, J. Phys. Chem., Vol. 43, p. 701 (1939).
4. T. H. James and W. Vanselow, PSA Journal (Phot. Sci. Tech.), Vol. 19B, p. 170 (1953).
5. A. Moyse, A. Ballard, and S. E. Sheppard, private communication (in these Laboratories).

6. T. H. James, Photographic Science and Technique, Vol. (II)2, p. 81 (1955).
7. H. Lüppo-Cramer, "Photographische Probleme," W. Knapp, Halle, 1907.
8. T. H. James, J. Phys. Chem., Vol. 47, p. 597 (1943).
9. T. H. James, J. Colloid Science, Vol. 4, p. 561 (1949).
10. G. W. W. Stevens, Phot. J., Vol. 82, p. 42 (1942).
11. T. H. James and W. Vanselow, J. Phys. Chem., Vol. 58, p. 894 (1954).
12. G. W. W. Stevens, private communication.

A RAPID SEQUENCE 70MM PRESS CAMERA

Charles A. Hulcher*

A SEQUENCE CAMERA designed specially for press photography was a dream of newspaper photographers discussed at the 1953 Rochester Photo Conference. At the Rochester meeting, which had been organized by the National Press Photographers' Association in cooperation with George Eastman House, camera manufacturers were urged to develop such a camera. The Charles A. Hulcher Company, manufacturers of high-speed 70mm cameras used by the armed forces for rocket and guided missile research recording, decided to accept the challenge.

Working in cooperation with some of the top press photographers of the country, the Hulcher organization developed a set of specifications for a news picture camera of the sequence type to meet the long existing need for a camera of that sort. The specification provided for pictures considerably larger than miniature camera size. They called for all the versatility of the commonly used press camera for still picture photography, plus the rapid sequence feature. These specifications were turned over to the camera designers to reduce to practice.

Using an intermittent film transport which had proved successful in their higher speed instruments, the camera designers completed the first two models in August 1954, less than a year after the Rochester Photo Conference ended. One of these was sent to the Nashville Tennessean for field testing and the other to Life magazine. Eight additional cameras followed and were placed in the hands of interested news picture organizations.

The experiences of these first ten camera users with the new equipment proved extremely helpful to the Hulcher organization in working out the "bugs" which every designer expects to encounter when his models first encounter the test of use in the field.

Specifications of the Camera

This new camera produces pictures $2^1/_4$ by $2^1/_2$ inches in size on doubly-perforated 70 mm film supplied in 100 foot long rolls. Single exposures may be made or series of pictures in sequence at intervals from 5 per second progressively to 20 pictures per second. One roll of film produces 470 pictures. Operation of the camera is powered normally by a 12-volt battery but provision can be made to operate on other voltage supplies.

The camera weighs $12^1/_2$ pounds when equipped with a $6^3/_8$" Wollensak Raptar f/4.5 lens in focusing mount. The 12-volt battery weighs $4^1/_2$ pounds and normally is carried slung over the photographer's shoulder. Two spade type handles, located at the center of gravity on each side of the camera, provide balance and security for hand-held operation. Tripod mounting means are provided, as shown in Figure one.

Exposures are metered by a rotary disc type shutter, operating close to the focal plane. This has an adjustable opening providing a range of exposures from $^1/_{25}$ sec. to $^1/_{2560}$ sec. The exposure time is selected and set by adjusting a pointer on the shutter shaft hub which extends through the front of the camera. These numbers run from 1 to 9. A chart attached to the camera, (see Table I), indicates the exposure obtained for various settings at different frame speeds.

In addition to the numbers indicated on the chart, speeds are infinitely variable and the shutter may be set between numbers in $2^1/_2$ degree increments.

Fig. 1. The 70mm rapid sequence camera, usually hand held for sports photography, is provided for tripod mounting. The operating trigger is conveniently located in relation to the luggage-type handles.

* Charles A. Hulcher Company, Inc., Hampton, Virginia. Received 12 September, 1955.

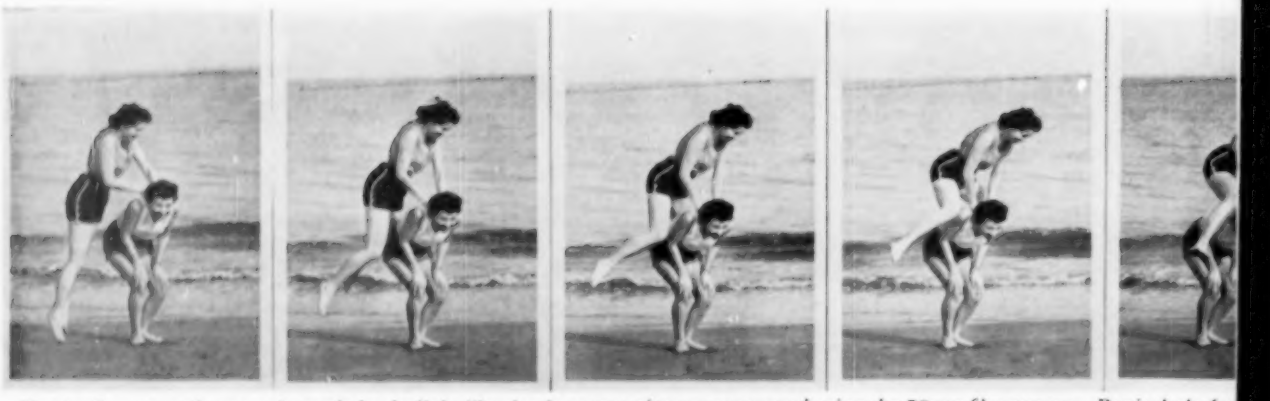


Fig. 3. Sequence photographs made by daylight illumination at ten pictures per second using the 70mm film camera. Particularly for the exposure too soon or too late. The relatively large size negatives provided by the 70mm wide film may be handled and printed like

Table I

EXPOSURE CHART FOR 70MM PRESS CAMERA

Shutter Setting	Frames per second 5	10	15	20
1	720	1440	2160	2880
2	360	720	1080	1440
3	180	360	540	720
4	90	180	270	360
5	60	120	180	240
6	45	90	135	180
7	36	72	108	144
8	30	60	90	120
9	25	50	75	100

Focusing of the lens is accomplished by means of a reflex system, using a front surface mirror and a full size ground glass screen. A small knob at the top of the camera rotates and locks the mirror in place for focusing. The mirror is automatically returned when the trigger is pulled to start the camera. A hood and magnifier aid in focusing. A heavy cast aluminum bayonet type snout provides for quick changing of lenses. The standard camera is equipped with a $6^{3}/_{4}$ inch f/4.5 Wollensak Raptar lens. Other lenses ranging from 3 to 80 in. focal lengths may be used with suitable adapters. Pre-set quick focussing lens mounts similar to the Big Bertha type are also available.

In addition to the reflex focusing system, the camera is equipped with a folding sports type viewfinder. Frame rates are set by turning a calibrated knob on the right hand side of the camera. A footage indicator is provided to inform the operator of the film supply remaining in the camera. Films having a wide range of emulsion types are now available from film manufacturers, including the new Kodak TRI-X Pan and Aero Ektachrome.

Operating Mechanism

Except for the reinforced plastic handles, the camera is constructed entirely of metal. The camera's unique operating mechanism provides intermittent film transport without the use of any reciprocating action. All moving parts revolve at a constant pre-set speed and only the film loop stops and starts. The film is held in a flat plane on all four sides and is not in motion during exposure. The path of the film inside the camera is illustrated in Figure two.

The supply spool is placed on Spindle A and the film is threaded behind Roller C, around the sprocket and Rollers D and E and then in an easy loop around Roller G, through the spring loaded pressure plate H and then around Roller I and back around the opposite side of the sprocket behind Rollers J and K, then onto the take-up

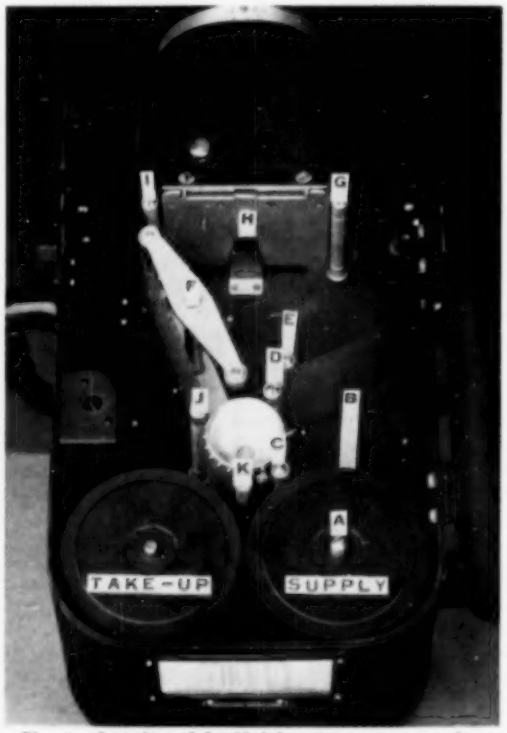
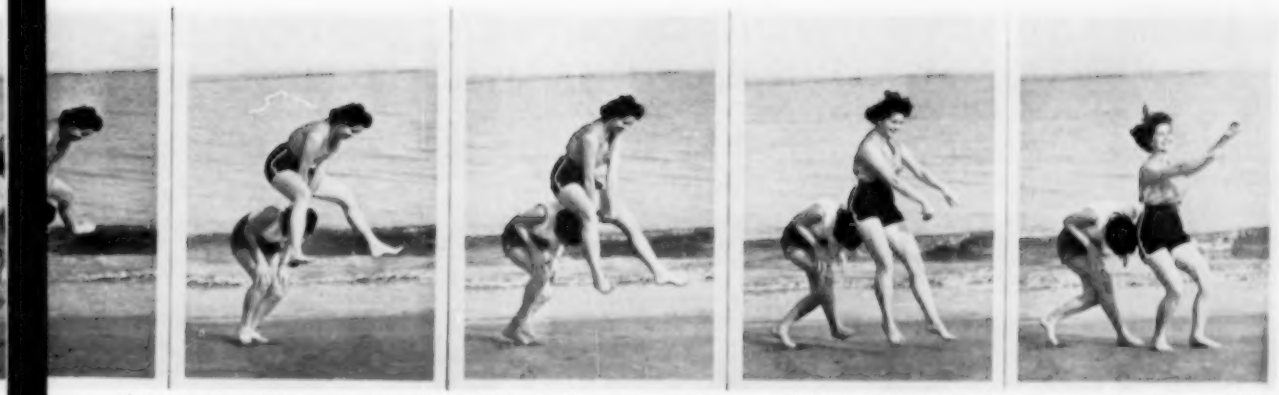


Fig. 2. Interior of the Hulcher 70mm camera showing the film path from the supply spool to the take-up spool and the rotating roller arms F, which provide the intermittent film advance.



hotographing sports events, newspaper photographers value a sequence camera which avoids missing important action due to making nventional press negatives.

spool. When the camera is started, film is fed from the supply spool by the sprocket on through the aperture and on back through the take-up spool at a constant preset rate. The intermittent motion of the film is caused by the rotation of the double roller assembly F which revolves at the same rate and in the same direction as the sprocket. The rotation of the Roller Assembly F changes the path of the film, pulling down the loop on the supply side of the film gate and then causing the film to stop in the gate after the Roller F has reached its maximum pull. The rotating disc shutter is geared to expose the film while it is in the stationary position. No pull down claws are used. A single shaft extending longitudinally along the camera, is geared to drive both the sprocket and the Roller Shaft F. The shutter is attached to one end of this shaft and the electric motor drives this shaft by means of a small chain belt. An adjustable centrifugal electrical governor controls the speed of the motor. No small or intricate parts are used.

Pulse or Single Frame Operation

By means of an electrical circuit and braking mechanism, the camera may be equipped to provide one picture each time the trigger is pulled. This system produces one frame only, regardless of how long the trigger is held down or how quickly it is released. It will recycle faster than the operator can pull and release the trigger. When so equipped, the camera may be used as a conventional still camera or with the flick of a switch, again operate as a sequence camera. The single-frame mechanism is enclosed in the camera body.

The camera may be pulsed remotely by means of a programer or by radio or other methods. Pulse rates up to 5 per second are possible with the standard motor However the principal use of the camera has been for recording sequences of action such as the series shown in Figure three.

Rapid Repeating Electronic Flash

A special fast repeating electronic flash system (Figure four) has been developed for use in conjunction with the camera. Known as "Sequi-Strobe," it was developed by

Fig. 4. Electronic flash unit provided for synchronized flash exposures with the 70mm sequence camera. Up to twenty pictures per second may be exposed with this equipment which operates on 115 volt A. C. power supply.

Mr. G. T. Strailman of Hampton, Virginia. This light source is synchronized with the camera at the factory. The light output provides a guide number of about 100 for Tri-X film. The light w ll flash up to 20 times per second. The power supply weighs 36 pounds and operates from 115 volts AC. The lamp may be mounted on the camera or set up where desired. When necessary, several lights may be used. The cover picture series was photographed by the use of the "Sequi-Strobe" in synchronization with the Hulcher 70 Press Camera at 20 pictures per second.

This 70mm rapid sequence press camera is currently being used by a number of newspapers, magazines, and news services. It is providing unusual and thorough coverage of news and sports events. The same features which make it useful in this field should also prove useful in other fields of industrial, research, and development photography.

GAMMA-RAY SENSITIVITIES OF SEVERAL BLACK-AND-WHITE NEGATIVE PHOTOGRAPHIC FILMS*

G. M. Corney

SUMMARY

Sensitivities to 1,000-kvp x-rays of twenty Kodak black-and-white negative materials were determined. Sensitivities so determined will also apply approximately to exposures to hard gamma rays (e.g., from radium or cobalt-60) and to the prompt radiation from an atomic bomb. The results may be used to estimate the density caused by inadvertent or unavoidable exposure to hard radiation and they also may be useful for disaster monitoring. Data from earlier work on six additional films are included.

THE INCREASING USE of nuclear energy and of radioactive isotopes has led to a concern among users of photography about the densities resulting from inadvertent or unavoidable gamma-ray exposures of photographic materials.

Data on the sensitivities of x-ray films to penetrating radiation, in terms of roentgens required to produce certain densities, are fairly complete,[1-5] since these films are commonly used in routine radiation monitoring.

The situation is quite different with respect to other photographic materials. Information in the published literature is scant and scattered. A few films, other than x-ray films, have been recommended for certain monitoring procedures, and their sensitivities have been published.[1-6] In addition, "radium tolerance exposures" of several films were determined in the course of setting up regulations for the shipment of radioactive substances.[7] The "radium tolerance exposure" is that exposure to the gamma rays of radium which will produce a just-perceptible density under certain specified exposure conditions.

It was, therefore, decided to measure the sensitivity to hard x-rays or gamma rays of twenty representative Kodak black-and-white negative films, chosen from all fields of photography, exclusive of radiography. Kodak black-and-white films for which satisfactory data already exist[1,6] were excluded from these tests, although the data for these films are included in Table III for ease in reference. The films investigated are listed below.

1. Eastman Background-X Panchromatic Negative Film
2. Eastman Fine Grain Duplicating Panchromatic Negative Film
3. Eastman Plus-X Panchromatic Negative Film
4. Kodak Commercial Film
5. Kodak Commercial Ortho Film
6. Kodak Contrast Process Ortho Film
7. Kodak Contrast Process Panchromatic Film
8. Kodak Infrared Aerographic Film
9. Kodak Linagraph Ortho Film
10. Kodak Linagraph Pan Film
11. Kodak Panatomic-X Film
12. Kodak Plus-X Panchromatic Film
13. Kodak Portrait Panchromatic Film
14. Kodak Royal Pan Film
15. Kodak Super Ortho-Press Film
16. Kodak Super-XX Aerial Recon R.P. Film
17. Kodak Super-XX Aerographic Film
18. Kodak Tri-X Aerial Recon Film
19. Kodak Tri-X Panchromatic Film
20. Recordak Micro-File Panchromatic Film

* Communication No. 1745 from the Kodak Research Laboratories, Rochester 4, New York. Received 24 August, 1955.

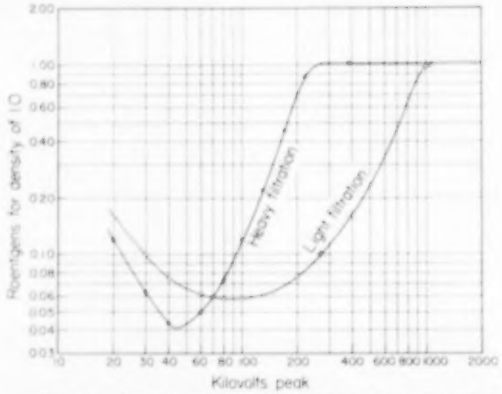


Figure 1: After Wilsey.[1] Roentgens for a density of 1.0 as a function of x-ray tube voltage, for light and heavy filtration, on Kodak Blue Brand X-ray Film. Points corresponding to the two radiation qualities used in this investigation are marked with crosses. (Courtesy of *Radiology*)

Procedure

The heterogeneous x-radiation generated at 1,000 kvp by a resonance transformer x-ray machine was used as a representative hard radiation. The data of Wilsey,[1] confirmed by other workers,[8,9] indicate that the sensitivity of a particular photographic material is essentially the same for all radiations harder than that generated at 1,000 kvp (Figure one). Thus, the sensitivity of a film to 1,000-kvp x-rays will represent fairly well its sensitivity to the gamma radiations from radium or cobalt-60, or to the prompt radiation from an atomic bomb.[9]

Previous experience has shown, and these experiments confirm, that the *shape* of the characteristic curve of a film exposed to x- or gamma rays is very little affected by the quality of the radiation, even though the *position* of the curve along the exposure axis is dependent on the quality. Since sensitometry with 1,000-kvp x-rays involves considerable experimental difficulty, it was thought proper, for the purposes of these tests, to obtain the curve *shape* from 250-kvcp sensitometric exposures and to use the densities obtained from 1,000-kvp flash exposures to *position* these curves properly along the logarithm-of-roentgens axis.

Sensitometric exposures were made on each film to radiation generated at 250 kvcp, filtered through 1 mm of copper, and flash exposures were made to known

Table I

ROENTGENS OF 1,000-KVP X-RAYS VS DENSITY

(Kodak Rapid X-ray Developer, 5 min.)

Kodak Film	Approximate Roentgens for Density of 0.3 + Fog	1.0	1.5	2.0	3.0	4.0
(1) Background-X	3.0	8.0	12.	32.	105	540
(2) Fine Grain Duplicating Pan	120.	240.	420	600	1250	...
(3) Plus-X Pan	2.0	4.6	12.	25.	130	1600
(4) Commercial	2.6	12.0	27.	58.	200	640
(5) Commercial Ortho	1.5	6.4	15.	31.	100	...
(6) Contrast Process Ortho	2.0	6.9	11.	18.	32	52
(7) Contrast Process Pan	4.9	16.	26.	39.	76	...
(8) Infrared Aerographic	1.2	3.9	8.4	16.	...	...
(9) Linagraph Ortho	1.1	3.0	6.3	10.2	31	100
(10) Linagraph Pan	0.66	1.4	4.0	10.7	170	...
(11) Panatomic-X	2.3	9.7	20.	37.	120	850
(12) Plus-X Pan	1.2	5.9	13.	27.	155	...
(13) Portrait Pan	1.9	7.1	20.	55.	520	...
(14) Royal Pan	1.0	3.7	10.	28.	540	...
(15) Super Ortho-Press	1.0	4.0	9.3	20.	174	...
(16) Super-XX Aerial Recon	1.0	4.3	10.0	20.	...	...
(17) Super-XX Aerographic	1.3	4.4	9.3	18.	100	...
(18) Tri-X Aerial Recon	0.50	3.6	5.1	20.	...	...
(19) Tri-X Pan	1.0	4.8	16.	56.	...	...
(20) Recordak Micro-File	46.	140.	230.	350.	670.	...

Table II

ROENTGENS OF 1,000-KVP X-RAYS VS DENSITY

Kodak Film	Kodak Developer	Time (min)	Approximate Roentgens for Density of 0.3 + Fog	1.0	1.5	2.0	3.0	4.0
(1) Background-X	D-76	8	5.2	70	150	1200	...	...
(2) Fine Grain Duplicating Pan	D-76	6	140	1150	...	...	...	...
(3) Plus-X Pan	D-76	8	3.7	19	100	450	...	...
(4) Commercial	DK-50	5	4.3	47	130	305	1400	...
(5) Commercial Ortho	DK-50	5	3.4	34	100	250	...	...
(6) Contrast Process Ortho	D-11	5	3.6	13	22	33	66	112
(7) Contrast Process Pan	D-11	5	11.5	36	63	98	200	...
(8) Infrared Aerographic	D-19	9.6	1.2	4.0	9.2	18	...	...
(9) Linagraph Ortho	D-19	7	1.1	3.2	6.5	12	36	130
(10) Linagraph Pan	D-19	7	0.54	1.8	5.8	16	...	...
(11) Panatomic-X	DK-50	5	5.0	41	122	380	...	...
(12) Plus-X Pan	DK-60a	7	1.8	8.9	28	85	...	...
(13) Portrait Pan	DK-50	5	5.2	52	190	600	...	...
(14) Royal Pan	DK-60a	4	1.2	13.2	79	440	...	...
(15) Super Ortho-Press	DK-60a	5	1.3	8.3	29	88	...	...
(16) Super-XX Aerial Recon	D-19	9.6	1.3	4.4	9.7	21	...	...
(17) Super-XX Aerographic	D-19	9.6	1.2	3.8	8.3	17	80	...
(18) Tri-X Aerial Recon	D-19	9.6	0.60	2.5	4.1	13	132	...
(19) Tri-X Pan	DK-60a	7	1.2	10.8	60	310	...	...
(20) Recordak Micro-File	Kodagraph	5	90	220	440	560	...	...

amounts of 1,000-kvp x-rays. All exposures were measured in terms of roentgens with a Victoreen condenser-type r-meter, using a bare 25-r chamber. Films exposed to the two radiations were developed together, with both a recommended development for the film in question and also 5 minutes' development in Kodak Rapid X-ray Developer. The latter development was chosen since Kodak Rapid X-ray Developer, or a similar product, is commonly used in routine photographic monitoring of radiation. The data may therefore be useful for emergency disaster monitoring.[6] All processing was done in deep tanks, with fresh developer, ASA agitation,[10] and a temperature of 68 F. Figure two is typical of the results obtained. The curves were drawn from 250-kvcp sensitometric data and were translated horizontally until they coincided with the marked points obtained from independent exposures made at 1,000 kvp. The marked points fall very well along the solid curves. This justifies the assumption that characteristic curve shape is relatively unaffected by radiation quality.

Results

Results are shown in Tables I and II, which correlate exposure in terms of roentgens of 1,000-kvp x-rays with photographic density. In Tables I and II, Column 4 shows the exposure required to produce a net density of 0.3. The succeeding columns are based on gross densities, including fog and the density of the support. Table III contains data available in previous publications,[1,6] and is included here for the sake of completeness and ease of reference.

Table III

ROENTGENS VS DENSITY

A. After Wilsey[1]

Film	Kodak Developer	Time (min)	Approximate Roentgens of Radium Gamma Rays for Density of 0.2 + Fog	1.0	2.0	3.0	4.0
Eastman Fine Grain Release Positive Safety Film, Type 7302	Kodak Rapid X-ray	5	22	100	225	400	750

B. After Corney and Clear[6]

Film	Kodak Developer	Time (min)	Approximate Roentgens of 1,000-Kvp X-rays for Density of 0.5	1.0	1.5	2.0	2.5	3.0
Kodak Super Panchro-Press Film, Type B	Kodak Rapid X-ray	5	1.3	4.3	11	30	85	280
Kodak Super-XX Panchromatic Film	"	5	1.4	4.7	13	35	110	440
Kodak Verichrome Film	"	5	1.9	5.4	14	43	...	...
Kodak Super Panchro-Press Film, Type B	DK-60a	6	1.7	7.6	27	87	280	1000
Kodak Super-XX Panchromatic Film	DK-60a	5.5	1.9	9.8	38	140	470	1300
Kodak Verichrome Film	DK-60a	7	2.1	6.9	22	83	...	...
Kodalith Ortho Film, Type 2	Kodalith	2.25	1100	1400	...	1700	...	1900

The sensitivities of these films to 1,000-kvp x-rays are approximate values. Since they are not normally tested for use with this radiation, their sensitivity to x-rays may be changed in the future, even though their sensitivity to light is maintained constant within the limit of manufacturing tolerances.

For radiations softer than 1,000-kvp x-rays, the speeds of photographic materials (in terms of the reciprocal of the number of roentgens required to produce a given density) increases as shown in Figure one. The shape of the radiation quality *vs* sensitivity curve was not determined for these films. However, comparisons of the absolute speeds, in terms of reciprocal roentgens, for 250-kvcp and 1,000-kvp radiations suggest that the sensitivity curves for all films tested may be of the same general shape as that of Figure one.

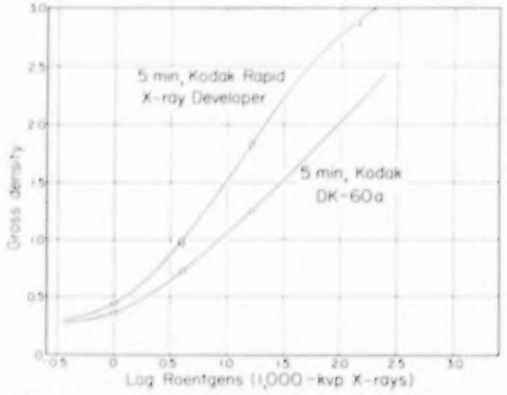


Figure 2: Characteristic curves of Kodak Super Ortho-Press Film. The solid lines represent 250-kvcp sensitometric curves, which were translated parallel to the log-roentgens axis until they coincided with the marked points (○) for the 1,000-kvp exposures.

Conclusions

The data of Tables I through III apply to fresh films and to the specific processing conditions used. However, within these limitations, they may be used to estimate the densities that will be produced on black-and-white negative materials by exposure to 1,000-kvp x-rays, gamma rays of radium or cobalt-60, or the prompt radiation from an atomic bomb. Phrased differently, they may be considered to apply to radiations whose *effective energy* is greater than 0.2 mev.[1]

References

1. Wilsey, R. B., "Use of Photographic Films for Monitoring Stray X-Rays and Gamma Rays," Radiology, Vol. 56, p. 229, 1951.
2. Taylor, L. S., "Measurement of X- and Gamma Radiation over a Wide Energy Range," Brit. J. Radiol., Vol. 24, p. 67, 1951.
3. Ehrlich, M., and Fitch, S. H., "Photographic X- and Gamma Ray Dosimetry," Nucleonics, Vol. 9, No. 3, p. 5; Vol. 9, No. 6, p. 12, 1951.
4. Herman, W. C., "New Film Packet for Radiation Dosimetry," Nucleonics, Vol. 9, No. 4, p. 74, 1951.
5. Ehrlich, M., "Photographic Dosimetry of X- and Gamma Rays," Nat. Bur. Standards Handbook 57, Supt. of Documents, Washington 25, D.C., 1954.
6. Corney, G. M., and Cleare, H. M., "Disaster Monitoring with Amateur and Commercial Photographic Films," Nucleonics Vol. 13, No. 8, p. 40, 1955.
7. Evans, R. D., "Physical Biological Administrative Problems Associated with the Transportation of Radioactive Substances," Nat. Acad. of Sciences, Nat. Research Council, Washington, D.C., 1951.
8. The x- and gamma-ray response curve of x-ray films has been determined by a number of workers with essentially the same results. The following are two selected references to such investigations:
   a. Ehrlich, M., and Fitch, S. H. (See Reference 3).
   b. Deal, L. J., Roberson, J. H., and Day, F. H., "Roentgen Ray Calibration of Photographic Film Exposure Meters," Amer. J. Roentgenol., Vol. 59, p. 731, 1948.
9. "Effects of Atomic Weapons," Supt. of Documents, Washington 25, D.C., 1950.
10. American Standard Z38.8.3-1947, "American Standard Practice for Photographic Processing Manipulation of Films and Plates," American Standards Assoc., New York, N.Y.

COPRECIPITATION OF SILVER BROMIDE WITH SILVER IODIDE AND WITH SILVER CHLORIDE*

C. R. Berry and S. J. Marino

ABSTRACT

The x-ray diffraction method was used to determine the composition of the mixed-crystal phases produced by running silver ions into a solution containing a mixture of halide ions. Some effects of variations of the temperature of precipitation and of the kind of colloid present were investigated.

First additions of silver caused the least-soluble component of the mixture to precipitate first: pure silver iodide in the silver bromoiodide system, and in the chlorobromide system, a phase having a composition in the range of 98 to 99 mole percent bromide. During the later stages of precipitation, a large amount of solution and redistribution of the initial precipitate occurred. The rate of reaction of the initial precipitate with the crystals precipitating later in the run was increased by raising the temperature or solvent concentration. Polyvinyl alcohol decreased the rate of reaction of the components. Gelatin increased the rate of reaction, in spite of the demonstration that it hindered the motion of ions in solution. This decrease in mobility is apparently counterbalanced by an increased rate of reaction associated with a much larger reactive surface (fine-grain size) of the initial precipitate.

In no case did any of the precipitates reach the equilibrium state, which would be a single homogeneous phase, even after ripening for times of about an hour. A small amount of the least-soluble silver halide component in a precipitate was not detected by the x-rays and was probably present in a finely divided state but was incorporated in the larger grains.

Although there are a number of ways of producing mixed crystals of the silver halides, one of the simplest is the scheme, described by Trivelli and Smith,[1] in which silver ions are introduced into a vessel containing a mixture of halide ions. A very powerful scheme for investigating the results of such a precipitation process is the x-ray diffraction analysis of the compositions of the crystalline phases present. Wilsey[2] first showed by this technique that iodide ions could replace bromide ions in the silver bromide structure and the unit-cell dimension of such a mixed crystal was proportional to the concentration of the iodide ions up to the limit of solubility of iodide in solid silver bromide. In contrast to common analytical procedures which give only the average composition when several phases are present, the x-ray diffraction method can measure, within limits, the relative amount and composition of each one.

In the experiments described here, the compositions were determined of the crystals produced by precipitation at various temperatures and in the presence or absence of gelatin. To interpret the results, it was necessary to consider the reactions that occur when phases of different compositions are present with a solvent, and some reactions of this kind were observed when separately prepared crystals of two different compositions were mixed.

Wilsey[2] showed that mixtures of any proportions of silver bromide and silver chloride formed homogeneous crystals of a single composition when cooled from the melt. Similarly, we have found, in agreement with Eastman and Milner,[3] that the equilibrium which is approached by silver chlorobromide crystals in potassium chloride solution is a single, homogeneous phase. For silver bromoiodide in potassium bromide solution, the equilibrium consists of a single phase for iodide concentrations up to about 40 mole percent, but at higher concentrations two phases result, as shown in Figure one. Raynaud and Pouradier[4] arrived at similar results and concluded that the two-phase system extends from iodide concentrations of 42 to 96 mole percent. Although these are the equilibrium conditions toward which the final precipitates must tend, it will be of interest to determine the actual state of the precipitates between the two extremes of homogeneous solid solution and separate phases of pure components.

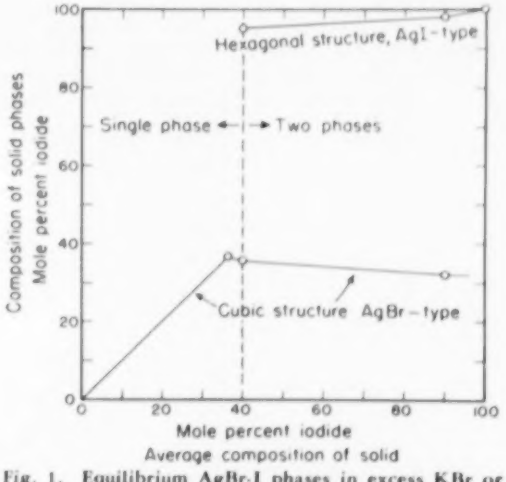


Fig. 1. Equilibrium AgBr-I phases in excess KBr or NH_4.

Experimental Procedures

A typical precipitate of silver bromoiodide was prepared at a specified temperature in the following manner: 10.0 grams of silver nitrate dissolved in 50 ml of water were run slowly (for about 30 min) into a beaker containing 1.17 grams of potassium iodide, 7.60 grams of potassium bromide, and 3.3 grams of gelatin dissolved

* Communication No. 1751 from the Kodak Research Laboratories, Rochester 4, New York. Received 19 September, 1955.

in 100 ml of water. This mixture resulted in a precipitate having an average composition of 12.0 mole percent iodide and left an excess of 9.5 grams per liter of potassium bromide (20 percent excess) in solution.

To prepare specimens for x-ray examination, a few drops of the solution with precipitate were put into some cold water to arrest ripening, and then the grains were separated from the liquid by centrifuging. The diffraction patterns produced with copper $K\alpha$-radiation were recorded on film in a Straumanis-type camera.[5] The compositions of phases were determined directly from lattice-parameter measurements, by using the linear relation between composition and lattice parameter which Wilsey[3] first demonstrated, but with more recently determined values of lattice parameter.[6]

The precision of composition measurements was usually about ±0.2 mole percent, but, in some cases where the diffraction lines were broadened by fine-grain size or by a distribution of compositions, the uncertainty was about ten times greater. In some instances, a small amount of material which was known to be present in a specimen could not be detected in the diffraction pattern. This is commonly the case in x-ray diffraction experiments when the phase constitutes less than about 5 percent of the total sample, particularly if the crystal size is rather small (less than 200 A.).

Results

In accordance with the usual analytical results, the first additions of silver ion to a mixture of bromide and iodide ions gave a precipitate which was essentially pure silver iodide until nearly all the iodide was precipitated. There may have been some bromide ions incorporated in the hexagonal silver iodide structure, but not more than a few tenths of a mole percent. In the early stages of mixed chlorobromide precipitation, there is a single phase having a very high bromide content, but containing from 1 to 2 mole percent of chloride. The results in Table I show that only small changes are produced in the composition of the initial precipitate in the silver chlorobromide system by changes of temperature, colloid, and the relative amounts of chloride and bromide ion.

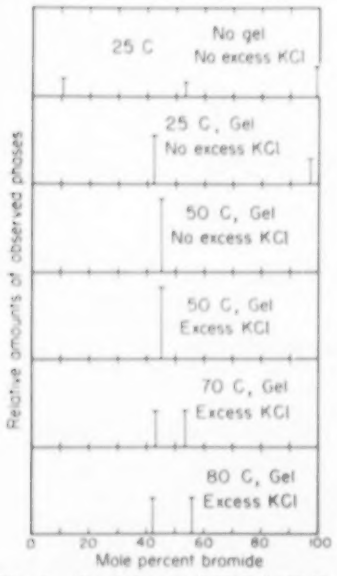


Fig. 2. Precipitates of 50% AgCl-Br.

Following the precipitation of the least-soluble silver halide component, the other component will precipitate. If no reaction occurred between the crystals precipitating during the earlier and later parts of the runs, we should expect to find two phases of widely different compositions. For example, with a silver chlorobromide precipitate having an average composition of 50 mole percent silver bromide, there would be approximately equal amounts of two phases having the compositions

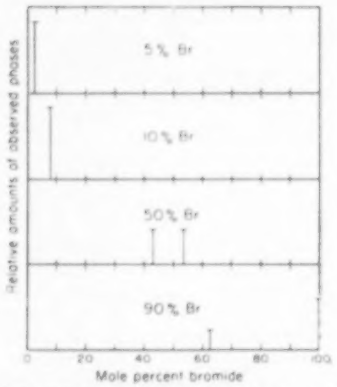


Fig. 3. Precipitates of AgCl-Br, at 70 C, 20% excess KCl, gelatin as colloid.

98.5 and zero mole percent silver bromide, respectively. The phases actually observed at the ends of such runs are shown in Figure two. It is clear that, in every case except at 25 C, a considerable amount of redistribution of the initial precipitate containing about 99 mole percent bromide occurred during the later parts of the runs. At temperatures of 50 C and higher, there was no longer any evidence of the initial precipitate. On the other hand, the equilibrium condition of a single phase of 50 mole percent silver bromide composition was not attained. Although only a single composition was observed at 50 C, it is clear that a small amount of material having a high concentration of bromide must have been present, though it was not detected in the diffraction patterns, in order to account for the average composition of 50 mole percent bromide that was always observed after prolonged ripening. Ordinary ripening times, such as 30 minutes, made only small changes from the compositions shown in Figure two.

Several silver chlorobromide precipitates were made in gelatin, at 70 C, with 20 percent excess potassium chloride and with different amounts of bromide. These results are shown in Figure three. In every case, there was a considerable amount of redistribution of the initial precipitate which contained approximately 99 mole percent bromide. But in no case was the bromide completely redistributed to form a single phase of the equilibrium composition. Keeping the precipitates at

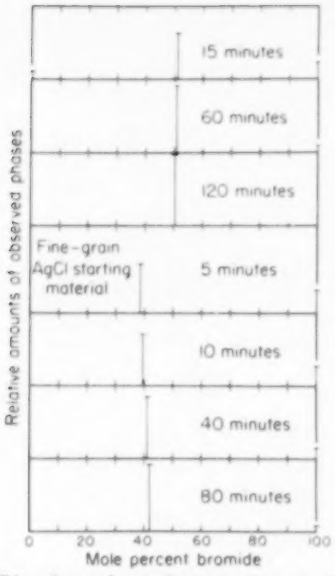


Fig. 4. Ripening of equal parts of pure AgBr and AgCl, at 50 C, and 6 grams per liter of KCl.

70 C for an additional half hour following the runs made only slight changes in the compositions. The compositions are somewhat nearer to the equilibrium in the chlorobromide system, however, than for the iodobromide system which will be described.

In view of the considerable amount of reaction which occurs between the phases existing in the precipitates during the runs, it was of interest to investigate the ripening reaction between preformed grains of silver bromide and silver chloride. For this purpose, pure bromide and pure chloride precipitates were made in gelatin. These grains were then mixed in a solution containing 6 grams per liter of potassium chloride and 2.2 percent gelatin at 50 C, which is a more dilute potassium chloride solution than that encountered during the precipitation. The extent of the reaction at various times is shown in Figure four. The lowest four graphs differ from the top three in that they refer to an experiment in which the grain size of the silver chloride used as the starting material was much smaller, owing to a much more rapid precipitation. Clearly, the course of reaction is altered by the grain size of the starting components. This is quite reasonable since the course of reaction must be determined by the rates of nucleation and growth of new phases which, in turn, depend on the rates of solution of the phases which are disappearing. Although the reaction shown in the lower part of Figure four resulted in nearly the same crystalline phases as the precipitate made at the same temperature, gelatin concentration, and excess of potassium chloride (Figure two), it was not generally possible to reproduce the result of a precipitation by reacting preformed grains of pure components.

In the production of sensitive emulsions, the silver bromoiodide system containing only a few mole percent of iodide is of particular interest. In order to make the reactions involved more evident, a higher concentration of iodide, 12.0 mole percent, was used in many precipitates. Results which were obtained in the absence of gelatin are shown in Figure five. At 25 C, with no excess potassium bromide remaining at the end of the precipitation, only pure silver bromide and silver iodide were present. The reaction between the pure phases under these conditions is very slow. In most of the precipitations, a 20 percent excess of potassium bromide (amounting to 9.5 grams per liter) was used. Increasing either the potassium bromide concentration or the temperature causes the reaction to accelerate. The amounts of pure silver bromide and pure silver iodide present at the end of the run become smaller as the temperature of the precipitation or the excess of potassium bromide is increased. But, in every case, pure silver bromide was the major phase present at the end of the 30-minute run.

Table I

COMPOSITION OF AgCl-Br PRECIPITATES AFTER PARTIAL ADDITION OF $AgNO_3$

°C	Colloid	Excess Cl	Fraction of $AgNO_3$ Added	Composition of Precipitate, Mole % Br	Average Composition of Precipitate after Addition of All the $AgNO_3$ Mole % Br
25	None	None	0.40	98.8	50
25	Gel	None	0.40	98.7	50
50	Gel	None	0.40	98.9	50
50	Gel	20%	0.40	98.7	50
70	Gel	20%	0.40	98.4	50
80	Gel	20%	0.40	98.2	50
70	Gel	20%	0.80	99.0	90

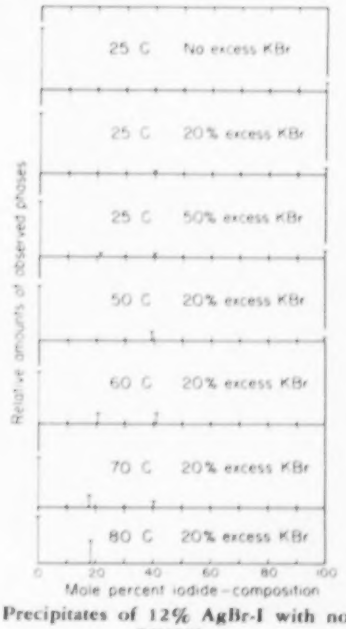


Fig. 5. Precipitates of 12% AgBr-I with no gelatin present.

Similar precipitations were made in polyvinyl alcohol at somewhat higher temperatures. The polyvinyl alcohol concentration was 80 grams of 16 percent polyvinyl alcohol per liter. The results are shown in Figure six. The net effect of the polyvinyl alcohol is to retard the reaction of the silver bromide and the silver iodide. Even at 80 C, some pure silver iodide was still present. On the other hand, the course of the reaction is somewhat different from that in the slow reactions observed with no colloid at low temperatures, since the polyvinyl alcohol encourages the growth of phases having compositions near zero percent iodide but definitely different from zero.

Results for a number of precipitations made in gelatin at different temperatures are shown in Figure seven. A comparison of these results with those found when no colloid was present indicates that at 25 C there is little difference; practically no reaction of the pure iodide and pure bromide occurred in either case.

At 50 C and higher, the reaction proceeded considerably further in gelatin than without the gelatin. At 70 C and 80 C, the precipitates formed in gelatin had very little resemblance to those made in the absence of gelatin. The results have been plotted in such a way as to emphasize the wide distribution of phases observed with gelatin. The reaction of the pure silver bromide is so rapid that none is apparent at the end of a run in gelatin, even though it is the major phase in the absence of gelatin. Although the rapid disappearance of silver iodide was somewhat unexpected, James and Vanselow[7] have now shown that the rate of solution of silver iodide is only about five times smaller than that of silver bromide under these conditions. Ripening of the precipitates made at 70 C and 80 C for an hour made little change in the phases observed.

Additional precipitates of silver bromoiodide having compositions from 1 to 15 mole percent iodide made at temperatures of 70 C and 80 C always had in common the feature, indicated in Figure seven, that the major phase contained only about half as much iodide as is known to be present. The other half of the silver iodide must be present in a form not detected in the diffraction patterns. This indicates that it may be in the form of a small number of silver iodide crystals of very fine grain size.

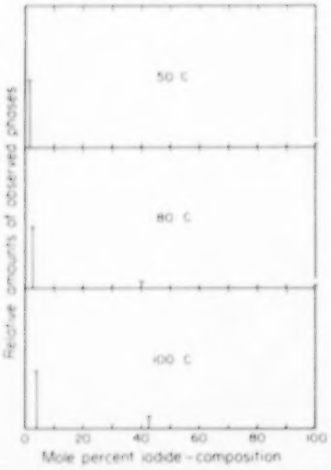


Fig. 6. Precipitates of 12% AgBr-I in P.V.A., 20% excess KBr.

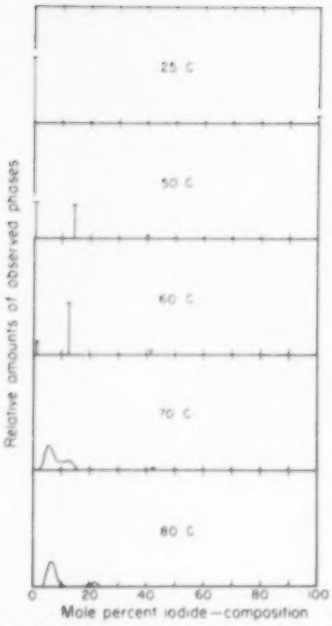


Fig. 7. Precipitates of 12% AgBr-I in gelatin, 20% excess KBr.

We suppose that this is the case, but, since grain-size fractions obtained by centrifuging failed to indicate any such phase, it must be either on the surface or in the grain boundaries of the larger crystals. Another indication that the unobserved iodide is connected with the large grains is an analysis which showed that the large grains have somewhat greater iodide content than the smaller ones.[8]

The acceleration of the reaction of silver iodide and silver bromide by precipitating in gelatin is interesting in view of the retarding influence which gelatin exerts on the Ostwald ripening of silver chloride grains.[9] To examine this situation more closely, observations were made of some reactions in potassium bromide solutions (320 grams per liter) at 50 C of preformed grains of different compositions in the presence and absence of gelatin. With 2.2 percent of gelatin present in the reacting solution, the time required to reach a given stage of reaction was about ten times greater than in the absence of gelatin. This is related to the retarding effect of gelatin on the diffusion of ions. But when both the precipitation of the preformed grains and the ripening reaction were carried out in gelatin, the reaction was about ten times faster than with no gelatin present. The accelerating effect which the gelatin has in this case appears to be related to the much larger reactive surface (finer grain size) of the two reacting components when precipitated in gelatin. This conclusion is based on electron-microscopic examinations[10] which showed that the grain sizes of the reactants prepared in gelatin were many times smaller than those prepared in the absence of gelatin.

It should be emphasized that the results found for these precipitates may not be applied to other precipitation schemes. For example, if a mixture of halide ions is run into a silver-ion solution, precipitates form which are very close to the equilibrium state.

Bibliography

1. A. P. H. Trivelli and W. F. Smith, Phot. J., Vol. 79, p. 330 (1939).
2. R. B. Wilsey, J. Franklin Inst., Vol. 200, p. 739 (1925).
3. E. D. Eastman and R. T. Milner, J. Chem. Phys. Vol. 1, p. 444 (1933).
4. H. Raynaud and J. Pouradier, J. chim. physique, Vol. 52, p. 133 (1955).
5. I. Ievins and M. Straumanis, Z. physikal. Chem., Vol. B33, p. 165 (1936).
6. C. R. Berry, Phys. Rev., Vol. 97, p. 676 (1955).
7. T. H. James and W. Vanselow, Phot. Sci. and Technique, in press.
8. W. D. Baldsiefen, V. B. Sease, and F. F. Renwick, Phot. J., Vol. 66, p. 163 (1926).
9. H. Ammann-Brass, Z. Naturforschung, Vol. 6a, p. 372 (1951).
10. C. Oster, of these Laboratories, private communication.

THE RATE OF PHOTOGRAPHIC DEVELOPMENT

T. H. James*

ABSTRACT

The rate of photographic development depends upon a number of factors. The rate is influenced by the nature of the developing agent, the concentration of the agent in the developer, the pH and temperature of the solution, the nature and the exposure of the photographic material, and various other agents which may be present in the solution. The purpose of the present paper is to discuss the reasons why these various factors affect the rate of development. No attempt has been made to give a complete survey of the literature, but references are given to original sources where the reader can obtain more detailed information on the points discussed.

The Developing Agents

A DEVELOPING AGENT must first of all be a reducing agent which is capable of reducing silver halide, i.e., the reaction must be thermodynamically possible. Reducing agents of widely different chemical structures can act as developing agents under proper conditions. Numerous attempts have been made to find a "rule of structure" by which developing agents could be characterized, but no general rule has been found. Organic developing agents often have a structure which can be represented by the Kendall formula,

$$a-(\mathrm{C}=\mathrm{C}-)_n-b,$$

where C is carbon, n is an integer, and a and b are the so-called active groups, —OH, —NH_2, —NHR, and —NRR′. This formula is not all-inclusive, however, even among the organic developing agents. The latter include such diverse structures as hydroquinone, *p*-aminophenol, catechol, *p*-phenylenediamine, various ring-substituted and N-substituted derivatives of these agents, ascorbic acid, oxyaminomesitylene, trioxymesitylene, 1-phenyl-3-pyrazolidinone, 1-phenyl-3-methyl-4-amino-5-pyrazolone, and leuco-bases of indophenols and indigotins. Most of the inorganic developing agents involve metals of variable valence. The simplest is vanadous ion. Others are complex ions containing ferrous iron, titanous titanium, chromous chromium, etc. The ferro-oxalate complex is the best-known example. Inorganic developers of other types are known, e.g., hydroxylamine, hydrogen peroxide, and sodium dithionite (hydrosulfite).

Several investigators have sought to characterize developing agents in terms of the redox (oxidation–reduction) potentials of the solution. The difference between the redox potential of the developing solution and that of the silver–silver halide system is proportional to the free energy of reaction in a reversible system, and the sign of the potential difference determines in which direction reaction can proceed (reduction of silver halide or oxidation of silver). In 1934, Reinders[1] showed, by varying the redox potential of a mixture of ferrous and ferric citrates or malonates in a solution containing 0.1 *M* KBr, that development of the latent image occurred only when the redox potential was more positive than −120 millivolts.† Abribat[2] arrived at substantially the same value from a study of other developer systems, but showed that the value depended to some extent upon the emulsion used. Abribat concludes[2] that every oxidation–reduction system with a real redox potential (reversible system) or an apparent redox potential (irreversible system) which is more positive than a certain critical value for a particular emulsion constitutes a possible developer, whatever the structure of the developing agent. However, the experiments of Abribat, Pouradier, and David[4] showed that the critical potential is the same for development of the latent image and for development of fog. In other words, they found that an agent which is capable of acting as a developer is also capable of reducing unexposed silver halide, as we should expect from thermodynamical considerations.

The action of the latent image, then, is to accelerate the reduction of the silver halide rather than to initiate a reaction which would not otherwise take place. In order to be a developing agent, a reducing agent must react with silver ions at a greater rate in the presence, than in the absence, of a latent image. The great majority of agents which will reduce silver halide at room temperature show developer action to some degree. If the reduc-

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† The sign used for the potential is adopted according to the Lewis and Randall convention (G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, N. Y., 1923).

tion of silver ions is not accelerated by silver nuclei, however, there is no basis for development of the usual kind. Furoin appears to be an example of an agent which reacts with silver salt at a rate unaffected by silver nuclei and is not a developer of the usual kind. Furoin reacts in the enol form to reduce the silver sulfite complex ion, and the rate of reaction is controlled by the rate of enolization.[5] The rate of reduction of the silver sulfite complex ion (or of the silver ion in equilibrium with it) by the enol form is much greater than the rate of formation of the enol form, and silver nuclei have no influence on the net rate of reduction. When tested under similar conditions, the rate of reduction of the silver sulfite complex by agents which are good developers is greatly accelerated by the presence of silver nuclei, and the rate of the reaction is determined by the concentration of silver ions rather than by the concentration of the silver sulfite complex.

Both the absolute rate of development and the ratio of the rate of development to that of fog formation vary considerably among the developing agents. Furthermore, the dependence of the rate of development upon the amount of exposure, the concentration of developing agent, the pH and temperature of the solution, and the presence of various addenda, such as sulfite, antifoggants, and quaternary ions, varies among the different developing agents. The agents fall into groups in relation to these properties, however. Levenson and James[6] have discussed the problem of classifying the developing agents according to certain common properties, and have shown that some order can be achieved if the developing agents are classified according to three characteristics: the sign and magnitude of the ionic charge on the active form of the agent, the chemical structure of the agent, and the strength and rate of adsorption of the agent by silver halide or silver. No one of these characteristics is sufficient in itself to account for the photographic behavior. Since this classification has been discussed in detail in a recent publication,[6] we shall not deal further with it here.

The Rate of Development

The rate of development is generally expressed either in terms of the rate of growth of density for a fixed exposure or in terms of the rate of growth of gamma. Rates measured from the growth of density are generally preferable for a basic study of the kinetics of silver formation. Such rates should be measured at several exposures extending over the major portion of the characteristic curve. Rates measured in terms of gamma are often preferred when the aim of the investigation is to get information on practical operating conditions of development.

Development may proceed with or without an induction period, according to conditions. The induction period in development may be defined as that stage at the start of development in which the rate of growth of density increases with time. The growth in density can result from an increase in the size of the developing silver particles, an increase in the number of developing or developed grains, or an increase in both. Development of certain positive-type emulsions, with the exposure in the shoulder region of the characteristic curve, follows closely the one extreme case in which growth of density results from growth in size of the developing particles.[7] The induction period measured from the density-time-of-development curve is representative of the induction period of the individual grain. At low exposures, the experimental evidence indicates that a rather wide range of induction periods exists among the various developable grains. Under such conditions, the induction period determined from the density curve represents a composite of the induction periods of those grains which have developed enough silver to contribute measurably to the density. A mixture of the two extreme methods of increasing density is represented in the intermediate exposure regions. To what extent this situation holds good for negative-type emulsions has not been determined.

Concentration of Developing Agent

The rate of development may vary in direct proportion to the concentration of the developing agent, or it may vary with a fractional power of that concentration,[8,9] i.e.,

$$\text{Rate} = B \cdot C_s^{\alpha},$$

where B is a constant, C_s is the concentration of developing agent in solution, and α is a fraction or one. The fractional power can be explained as a consequence of adsorption of the developing agent by silver halide or silver. If adsorption follows the Freundlich isotherm, the amount adsorbed varies with the amount in solution according to the relation,

$$C\ (\text{adsorbed}) = K \cdot C_s^{\alpha},$$

where K is a constant. According to this explanation, the rate of development is directly proportional to the amount of developer in the adsorbed state, but this amount varies as a fractional power of the amount present in the developer solution. Apart from the kinetic results, there is more direct evidence that silver bromide will adsorb a variety of developing agents. These agents, such as hydroquinone, hydroxylamine, and *p*-phenylenediamine, under proper conditions can displace adsorbed dyes from the silver bromide surface and hence must themselves be adsorbed by the surface.[10,11] In general, the conditions which favor displacement of the dyes are also those which favor development.

In some practical developers, the rate of development is nearly proportional to the concentration of developing agent. This may imply that adsorption is weak (α nearly unity), that the measured rate of development is determined by the rate of adsorption rather than by the equilibrium concentration of adsorbed material, or that the measured rate is determined by some diffusion process. Diffusion of the developer through the gelatin layer is the dominant factor under some development conditions.[12,13] This diffusion process is particularly important in very rapid development. The rate depends on the concentration gradient between the solution and the developing grains, and on local concentration gradients within the gelatin layer. In general, the rate of development controlled by diffusion will be proportional to the concentration of the developing agent in the solution.

A change of conditions of the solution can bring about a transition from a reaction-controlled rate to a diffusion-controlled rate, with an accompanying change in concentration-dependence. For example, when the exposure is in or near the shoulder region of the characteristic curve, the rate of development of motion-picture positive film by 1-phenyl-3-pyrazolidinone at pH 6.6 varies as the two-thirds power of the concentration of developing agent in the absence of bromide. Increase in pH to 9.5 is accompanied by a transition to a diffusion-controlled rate, and the rate at this pH varies with the first power of the concentration.[11] The pH region in which the transition takes place depends upon the exposure and also upon the temperature of the developer. Bromide, which slows down the chemical reaction, shifts the transition region to higher pH. Decrease in exposure, which lengthens the average induction period of the individual grain, has the same effect.

The degree of agitation of the developer influences the rate of development whenever diffusion is a factor. A change in the effectiveness of the agitation can cause a change in the shape of the characteristic curve, since the relative importance of diffusion can depend upon the amount of reaction taking place in a particular region of the emulsion, and this, in turn, depends upon the amount of exposure.

Temperature

The rate of most chemical reactions increases with increasing temperature, and development is no exception. The over-all effect of temperature on development is determined by one or more of the following factors: An increase in temperature increases not only the specific rate of the chemical reaction or reactions involved, but the degree of ionization of a developer which contains a hydroxyl group, and the rate of diffusion as well. An increase in temperature generally decreases the pH of the developer. The quantitative effect of temperature will depend upon the nature and exposure conditions of the photographic material, the nature of the developing agent, and the composition of the developing solution.

Under simple conditions, the specific rate of image development, v_i, for a particular exposure follows the Arrhenius equation, and can be expressed by the equation,

$$v_i = B_i \exp(-E_i/RT), \qquad (1)$$

where B_i is a statistical factor, E_i is the activation energy, R is the gas constant, T is the absolute temperature, and "exp" stands for the exponential function. The rate of fog development can be expressed similarly as:

$$v_f = B_f \exp(-E_f/RT), \qquad (2)$$

where B_f is a different statistical factor.

The temperature-dependence of fog formation is generally greater than that of image development,[12,13,14] that is, E_f is larger than E_i. Discrimination between latent-image development and fog becomes poorer as the temperature of development increases. However, the temperature-dependence of image development increases with decreasing exposure, and this means that the shape of the characteristic curve depends upon temperature. The rate of development in the low exposure areas is increased more by an increase in temperature than is the rate of development in the high exposure areas. The effective photographic speed accordingly increases with temperature if development is carried to a fixed gamma and if fog does not become excessive. If development is carried to a fixed fog level, speed decreases with increasing temperature. The quantitative relation between the amount of exposure and the temperature-dependence of development is not the same for all developing agents or even for a single developing agent and different compositions of the developer solution. Hence, the influence of temperature on speed and curve shape depends upon the developer used.

The temperature-dependence of practical developers varies considerably according to the composition of the developer and the material developed. Temperature coefficients ranging from about 1.25 to nearly 4 have been reported in the literature. Several factors determine the temperature coefficient under any particular set of conditions. Organic developers containing one or more hydroxyl groups appear to be more active in the ionized than in the nonionized form. The degree of ionization increases with increasing temperature, and hence the concentration of the more active form increases. The relative increase in concentration of the ion brought about by an increase in temperature will be larger in a pH region where the compound is only slightly ionized than in a higher pH region where it is nearly completely ionized. Hence, we should expect the temperature coefficient of development by such a compound to decrease as the pH increases.

Data obtained on a hydroquinone developer show a nearly quantitative agreement between the observed change of temperature coefficient with pH and that calculated from the change in ionization.[15] The temperature coefficient of development by Metol decreases with increase in pH.[14] At least a major portion of the change can be accounted for by a change in ionization. Burki and Jenny[16] determined the pH and temperature coefficients of a number of developers used in practice. They found that the temperature coefficient decreases continuously with increasing pH. The composition of these developers varied considerably, however, and a theoretical analysis of the results is not feasible.

The temperature-dependence of development by a solution which contains potassium bromide is greater than that of one which does not, provided diffusion is not the rate-controlling factor. Experiments with Metol developers show that the temperature coefficient increases with increasing bromide concentration at first, then levels off for these solutions.[14,17] Sugai and Furuichi[18] also found that the temperature-dependence of development by Metol increases with increasing iodide content of the silver bromoiodide emulsions used.

If conditions are such that diffusion controls the rate of development, the temperature coefficient is relatively low. The rate follows the Arrhenius equation, and the activation energies reported in the literature vary from 6.5 to about 8 kcal/mole.

An activation energy of this magnitude is not proof, however, that diffusion is rate-controlling. The apparent activation energy of the chemical reaction of some developers can be this small.

The temperature-dependence of development under a particular set of conditions varies with the developing agent used. Thus, Fortmiller and James found that the apparent activation energy of development of an exposed liquid emulsion by hydroquinone was about 8 kcal/mole and was independent of pH if the divalent ion is the active species, whereas the activation energies of development by Metol (corrected for ionization) was 10–11 kcal/mole, and by N^1,N^1-diethyltoluene-2,5-diamine was 21–22 kcal/mole.

If the developing agent is adsorbed by the silver halide before chemical reaction occurs, as seems probable, factors which influence surface conditions of the silver halide should have some influence on the heat of adsorption. The apparent activation energy, E_i, of Equation (1) includes a net heat of adsorption term. Hence, the temperature-dependence of development should be affected to some extent by the surface conditions of the silver halide. The influence of bromide on the activation energy may, in part, be determined by this effect. It is also possible that a change in pH will alter adsorption conditions to some extent. This latter point will be examined in more detail when we consider the effect of pH on the rate of development.

Influence of pH

Some inorganic developers are relatively insensitive to pH. A ferro-oxalate developer can be prepared which is nearly independent of pH over the range, 4 to 7, when the salt concentration of the solution is sufficient to suppress charge effects in the gelatin.[19] The vanadium developer is dependent on pH only so far as its solubility is concerned. The measured rate of development is independent of pH so long as conditions allow the vanadous ion to stay in solution,[20] but the rate is actually diffusion-controlled. The rate of development by certain other inorganic agents, such as hydroxylamine and hydrogen peroxide, is strongly dependent on pH.

The pH of the solution is a very important factor in determining the rate of development by most organic agents.[21,22,23] The pH-dependence of developers containing the hydroxyl group is largely determined by the ionization of that group, since the ionized form is the more active. Metol, for example, can ionize to form a univalent ion according to the equation,

$$CH_3NHC_6H_4OH \rightleftharpoons CH_3NHC_6H_4O^- + H^+, \qquad (3)$$

and the concentration of the ionized form follows the Ostwald dilution formula,

$$\frac{[CH_3NHC_6H_4O^-][H^+]}{[CH_3NHC_6H_4OH]} = K = 4 \times 10^{-11} \text{ at } 20\,C. \qquad (4)$$

The increase in activity of a Metol solution as pH increases is not quantitatively proportional to the increase in concentration of the ion. It may be that the nonionized form takes some part in development. However, another explanation is also possible.[24] Gelatin possesses a net negative charge in alkaline solution, and the magnitude of this charge increases with increasing pH in the region of 7.7 to 10.2. The negative charge of the gelatin impedes the diffusion of negatively charged developer ion through the gelatin layer surrounding the grain, and should act to decrease adsorption of the ion by the grain surface. At pH above 10, adsorption of hydroxyl ions by silver bromide may increase the negative charge at the silver halide surface and further discourage adsorption of negatively charged developing agents.[13] If the developer contains little or no bromide, the rate of development of an ordinary coated emulsion by Metol at pH 10 or above is, in part, determined by the rate of diffusion of the agent through the emulsion layer.[14] The measured rate of development is then less than the rate of chemical reaction.

Data on the rate of development by hydroquinone in the pH region 8 to 9.5 indicate that the major portion of the reaction is carried by the divalent ion. When charge effects of the gelatin and adsorbed hydroxyl ions are taken into consideration, it may be that the rate can be accounted for quantitatively by a reaction of the divalent ion. Quantitative data on the influence of these factors on the surface charge and on the specific adsorption of the developer ions are not available. The univalent ion of hydroquinone and even the nonionized form are active in physical development in neutral and mildly acid solutions, however, and it remains possible that the univalent ion may play some part in chemical development under suitable conditions, particularly in the induction-period region.

The *p*-phenylenediamines do not form active ions in the pH range of photographic interest, and hence an explanation of their pH-dependence must be sought elsewhere. Oxidation products of at least some of the *p*-phenylenediamine derivatives inhibit development. The increase in rate of development with increase in pH may be a consequence of an increased rate of decomposition of the oxidation product. This suggestion is supported by the fact that removal of the oxidation products in other ways, as by reaction with sulfite or couplers, likewise increases the rate of development. However, we must not overlook the possibility of a base catalysis involving the removal of a hydrogen ion from the complex formed between the diamine and silver ion. The curves obtained by plotting the logarithm of the development rate against pH for a series of derivatives of *p*-phenylenediamine have much the same shape, but are shifted along the pH axis from one another.[23] At high pH, all have about the same rate of development, but the measured rate then is almost entirely diffusion-controlled.

Elvegård[25] observed that the gamma developed by a Metol-hydroquinone developer could be represented by the equation,

$$\gamma = A \log t + B, \qquad (5)$$

where t is the time of development, A is a constant, and B increased with increasing pH. A plot of B against pH gave a curve composed of two straight lines which intersect at pH 9.7. He also observed that the confluence point, which lay well below the log E axis for the weakly alkaline solutions, shifted along a practically straight line toward the log E axis as the pH increased to about 10. Beyond 10, the confluence point moved irregularly somewhat below the log E axis in the direction of shorter exposures. This change in properties at about pH 10 did not depend on the concentration of developing agents, and Elvegård suggests that at pH 10 some hydrolysis of silver bromide occurs. The grains are no longer pure silver halide, but contain some oxide. The adsorption properties of such a surface would not be identical with those of the pure halide. Silver oxide, moreover, should

be more reactive toward the developer, and this could increase the rate of development of grains with relatively small latent-image centers. Lüppo-Cramer[26] has explained the fogging action of solutions of high pH on the basis of hydrolysis of the silver halide. The fogging action of developing agents at very high pH is generally greater than can be accounted for simply by increased activity of the developing agent, and hence must be associated with some change in the reactivity of the silver halide grains.

Effect of Sulfite

Sulfite is present in most of the developer formulas in common use. It is generally stated that sulfite is added as a preservative, but sulfite contributes in other ways to the properties of the developer, sometimes for the better, sometimes not.

When used in solution with some of the common developing agents, such as Metol and hydroquinone, sulfite prevents or greatly decreases the formation of oxidation products which would alter the rate of development. Oxidation products of hydroquinone, for example, accelerate development, while those of Metol and many of the derivatives of *p*-phenylenediamine retard development. A semiquinone is formed as an intermediate in the oxidation of these agents, and sulfite apparently reacts with this semiquinone to produce a sulfonate of the developing agent.[27] In this way, sulfite prevents the accumulation of oxidation products which could seriously influence the rate of development, accelerate aerial oxidation of the developer, and often stain the film. The monosulfonates are generally developing agents, but are less active than the parent agents. Some organic developing agents do not form sulfonates in this way. Ascorbic acid and 1-phenyl-3-pyrazolidinone are examples.

Sulfite exerts a solvent action on silver bromide and silver chloride. This solvent action can influence the course of development in a number of ways. If the exposed film contains a large amount of internal latent image, the solvent action of the sulfite will permit development of some of the internal latent image, particularly on prolonged development. Sulfite increases the equilibrium solubility of silver bromide. It also increases the rate at which silver bromide dissolves, although not in proportion to the increase in solubility.[28]

The amount of silver halide dissolved in sulfite in a given time will be influenced by reaction between the silver ion and the developer. Since this reaction is catalyzed by silver, some physical development of silver ions diffusing from nondeveloping grains may take place on adjacent developing grains, and this action will further promote solution of the nondeveloping grains. In a high-activity developer, such as the usual Metol-hydroquinone developer of pH above 10, the rate of this physical development is limited only by the rate at which silver ions arrive at the available silver surface, and this, in turn, is determined largely by the rate of solution of silver halide. In a low-activity developer, the rate of reduction of the silver ions at the silver surface also is involved, and the influence of sulfite on the equilibrium solubility can have an important bearing on the relative amounts of direct and physical development which occur. With a slow-acting developer, the solvent action of the sulfite may interfere with direct development by isolating the latent-image nuclei from the silver halide[29] and cause a major shift of the net development toward physical development. An extreme example of this action has been observed in studies of the effect of sulfite on development by hydroxylamine.[30]

Mild solvent action by sulfite appears to increase the relative rate of development of the grains in the low exposure region. Thus, a significant increase in emulsion speed, measured for a fixed gamma, has been observed when sodium sulfite is added to an ascorbic acid developer.[31] The increase amounted to ten-fold in some instances. Smaller effects in the same direction have been observed when the sulfite concentration of a Metol-hydroquinone developer is increased. Thus, Levenson[32] found that the speed obtained in a Kodak D-76-type developer which contained an addition of 1.0 gram of potassium bromide per liter was decreased from two- to three-fold by decreasing the sulfite concentration from 100 to 25 g. The solvent action of the sulfite probably either uncovers some internal latent image which is very near the surface or else decreases the induction period in the development of grains containing latent-image centers of near threshold size.

Other Manifestations of Surface Conditions

We have already made some reference to the effect of the charge of the silver halide surface on the rate of development. This charge has its origin in the fact that the silver halide grains in a normal emulsion have an excess of halide ions on the surface, which accordingly has a net negative charge. A negatively charged developer ion approaching such a grain will experience an electrostatic repulsion. To reach the surface, an ion must possess enough kinetic energy to overcome this repulsion. Calculation indicates that a univalent ion would need a kinetic energy of the order of 10^{-13} erg to reach the surface of a grain when the emulsion pAg is 8.0.[12] A divalent ion would need twice as much energy. These values are greater than the average energy possessed by an ion in solution at room temperature, and only a fraction of the ions will possess the required excess energy. The surface charge in effect decreases the available concentration of developing agent for reaction at the surface. As development of a grain progresses, the surface charge in the vicinity of the growing silver nucleus decreases because the halide ion is not held by the silver surface, and the effective concentration of developing agent increases. The gross induction period observed in development by negatively charged ions has been explained on this basis.[33]

It is probably too simple to consider the charge barrier only in terms of electrostatic repulsion at a distance. If the developer ion gets close enough to the surface, forces of adsorption will come into play. Also, the ionization of the molecules will be influenced by the ionic atmosphere surrounding the grain. The surface charge will tend to decrease adsorption of like-charged ions, and it appears quite possible to treat the charge effect primarily as an effect on adsorption.[6] The simple electrostatic repulsion treatment without reference to adsorption gives answers which are of the right order of magnitude,[12] but does not account for variations among agents of the same charge.

The action of certain dyes and quaternary salts, present either in the emulsion or in the developer, can be ac-

counted for on the basis of their influence on surface charge and adsorption. Any agent which influences the adsorption of the developer would be expected to alter the rate of development, and several examples of this influence have been treated in the literature.[34] These include the action of gelatin, halide ions, and antifoggants, as well as the dyes and quaternary salts mentioned above. Agents of like charge generally compete for adsorption sites. Agents of opposite charge may promote adsorption of developer ions. It appears that most strongly adsorbed agents of either sign interfere to some extent with adsorption of the uncharged developing agents. There is ample evidence to show that the surface conditions of the silver halide grains exert a significant influence on the rate of development. More detailed information will be needed, however, before the relation between surface conditions and reaction rate can be treated quantitatively.

Bibliography

1. W. Reinders, J. Phys. Chem., Vol. 38, p. 783 (1934).
2. M. Abribat, Science et inds. phot., Vol. 5, p. 140 (1935).
3. M. Abribat, Phot. J., Vol. 92B, p. 25 (1952).
4. M. Abribat, J. Pouradier, and J. David, Science et inds. phot., Vol. (2)20 p. 121 (1949).
5. T. H. James, J. Am. Chem. Soc., Vol. 62, p. 3411 (1940).
6. G. I. P. Levenson and T. H. James, J. Phot. Sci., Vol. 2, p. 169 (1954).
7. T. H. James, J. Franklin Inst., Vol. 240, p. 83 (1945).
8. T. H. James, J. Chem. Phys., Vol. 14, p. 536 (1946).
9. G. I. P. Levenson, J. Phot. Sci., Vol. 1, p. 117 (1953).
10. T. H. James and W. Vanselow, J. Am. Chem. Soc., Vol. 73, p. 5617 (1951); Vol. 74, p. 2374 (1952).
11. T. H. James and W. Vanselow, Phot. Sci. and Technique, Vol. (2)1, p. 77 (1954).
12. V. I. Shiberstoff, quoted in Mees, "Theory of the Photographic Process," 2nd ed., The Macmillan Co., New York, N. Y., 1954, p. 675.
13. T. H. James, Royal Photographic Society Centenary Intern. Conference on the Science and Applications of Phot.; London, September, 1953, p. 165.
14. T. H. James, Phot. Sci. and Technique, Vol. (2)2, p. 81 (1955).
15. L. J. Fortmiller and T. H. James, PSA Journal (Phot. Sci. and Technique), Vol. 18B, p. 76 (1952).
16. F. Bürki and L. Jenny, Helv. Chim. Acta, Vol. 26, p. 2264 (1943).
17. S. Sugai, J. Faculty Sci., Hokkaido Univ., Japan, Vol. (II)4, p. 268 (1953).
18. S. Sugai and J. Furuichi, Ibid., Vol. (II)4, p. 253 (1953).
19. T. H. James, J. Chem. Phys., Vol. 12, p. 453 (1944).
20. L. J. Fortmiller and T. H. James, Royal Photographic Society Centenary Intern. Conference on the Science and Applications of Phot., London, September, 1953, p. 161.
21. W. Reinders and M. C. F. Beukers, Ber. VIII Internat. Kongr. Phot., Dresden, 1931, p. 171.
22. F. Bürki and U. Ostwalt, Helv. Chim. Acta, Vol. 22, p. 30 (1939).
23. T. H. James, PSA Journal (Phot. Sci. and Technique), Vol. 16B, p. 83 (1950).
24. L. J. Fortmiller and T. H. James, PSA Journal (Phot. Sci. and Technique), Vol. 19B, p. 109 (1953).
25. E. R. Elvegård, Z. wiss. Phot., Vol. 41, p. 81 (1942); Vol. 42, p. 65 (1943).
26. H. Lüppo-Cramer, Phot. Korr., Vol. 73, p. 49 (1937).
27. J. E. LuValle, J. Am. Chem. Soc., Vol. 74, p. 2970 (1952).
28. T. H. James and W. Vanselow, Phot. Sci. and Technique, in this issue.
29. H. Lüppo-Cramer, "Photographische Probleme," W. Knapp, Halle, 1907, p. 157; T. H. James, J. Colloid Sci., Vol. 4, p. 561 (1949).
30. T. H. James, J. Phys. Chem., Vol. 47, p. 597 (1943).
31. T. H. James, J. Franklin Inst., Vol. 240, p. 327 (1945).
32. G. I. P. Levenson, Phot. J., Vol. 88B, p. 102 (1948).
33. T. H. James, J. Phys. Chem., Vol. 43, p. 701 (1939); J. Franklin Inst., Vol. 240, p. 83 (1945).
34. T. H. James and W. Vanselow, J. Phys. Chem., Vol. 58, p. 894 (1954).

DESIGN OF SAFELIGHT FILTERS

E. S. Mackey and L. A. Micco*

In photographic terminology, a safelight filter usually means a light source attenuator which can be used under darkroom conditions without the risk of fogging a specific type of photographic film or paper. It must be remembered, however, that although the filter by definition is called "safe," it is only safe when certain qualifications are considered, such as the time of exposure and the intensity of radiation employed; and, of course, the filter must be used with products for which it is specifically recommended. Photographic safelight filters are not only used for illumination during the processing and printing procedures but also are a necessity during the manufacturing, inspection, and packaging operations of sensitized goods production. In general, for any given sensitized material, a filter must provide a maximum absorption in that portion of the spectrum to which the film is most sensitive, yet transmit as much as possible of the remainder of the visible spectrum for darkroom illumination. In order to design filters for practical use, three basic factors must be considered:

1. The spectral sensitivity of the eye.
2. The spectral sensitivity of the photographic material.
3. The specific usage of the filter.

The spectral sensitivity of the eye has two parts. The first is assignable to the cones, whose sensitivity peaks at 555 millimicrons and extends well into the red region of the spectrum. The second part is assignable to the rods, whose sensitivity peaks at approximately 510 millimicrons. In other words, the rods are more sensitive to the short wavelength or blue part of the spectrum and the cones are more sensitive to the long wavelength or red part of the spectrum.

Daylight vision is almost wholly assignable to the cones while the rods are responsible for night-time vision. The transition from cone to rod vision is by no means a simple one. It has been found to be a function of the wavelength as well as the intensity of the light used. It is also known that the photosensitive pigment of the rods, called rhodopsin, is bleached out by daylight and requires approximately one-half hour of near darkness to rebuild to a proper concentration so that the rods will

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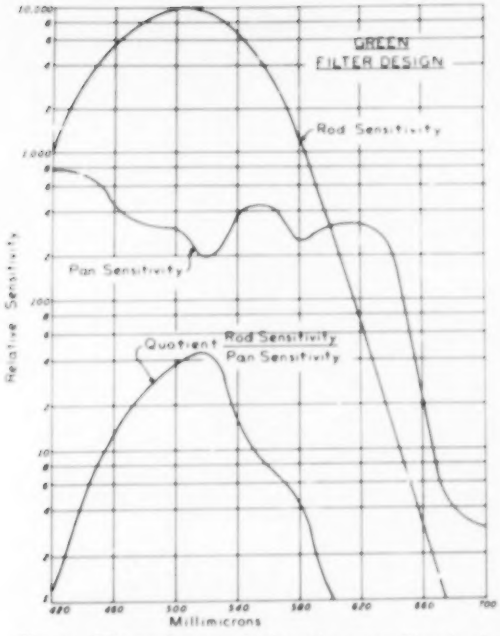

Fig. 1. The peak transmission of a green filter is obtained from the quotient of eye sensitivity divided by the film sensitivity.

again absorb light. This is why one is forced to adapt to darkness for such long periods of time when going into rooms of low illumination.

The spectral sensitivity of the film, which has been noted as the second factor is a very important requirement. Three major types of sensitivities may be briefly described as follows:

a. The group composed of optically unsensitized emulsions (blue sensitive emulsions).

b. The group in which sensitivity has been extended into the green portion of the spectrum (orthochromatic emulsions).

c. The group to which a red sensitivity has been imparted (panchromatic emulsion).

A consideration of the third factor, that of the use for which the filter is intended, comes into play when the filter designer has been requested to make a filter for a specific purpose. This requirement rarely affects the color of the filter, which is determined by the two previous factors, but does determine the level of illumination needed. For example, during some manufacturing procedures such as the slitting operation, the speed at which the film travels allows the use of a safelight providing a relatively high level of illumination. A hand inspection operation, which is a slower process, requires a filter with a lower level of illumination.

The first step in the design of a safelight filter for a panchromatic film would be to obtain a plot of the film's spectral sensitivity as shown graphically in Figure one. Since this film has sensitivity over nearly the entire visual spectrum and is known to be a high speed type, it is obvious that any usable filter would require such a low level of illumination that the rod or low brightness vision would be functioning. For maximum safelight efficiency, that is maximum safety with maximum visibility, a wavelength must be chosen where the sensitivity of the eye divided by the sensitivity of the film is a maximum. This can be shown in Figure one, where the relative sensitivity of a typical panchromatic material and the relative sensitivity of the rods are plotted. If the quotient of eye sensitivity divided by film sensitivity is obtained at 10 millimicrons intervals (as plotted in Figure one), it will be noted a maximum is obtained at 510 millimicrons. Therefore, a green filter should be chosen which has peak transmission at this wavelength. This is the familiar dark green filter which is often used in handling panchromatic black and white materials.

Although the most efficient wavelength band to use for the filter is now known, numerous tests must still be run to determine the light intensity permissible for a given lamp to film distance and for specific exposure times. For extra fast panchromatic materials the safe time must be short and the safe intensity must be low in order to avoid fogging. Often it is necessary to wait until development is well along before any appreciable quantity of light can be used.

Surprising as it may seem there are certain applications where a red filter is preferable to a green filter for use even with panchromatic film. For example, a person entering a dark area from outdoors depends on cone vision until the rod pigment can be rebuilt to the proper concentration. During this time, his eye is still sensitive to red light. A red filter, designed from data which are shown in Figure two, takes advantage of the eye sensitivity and

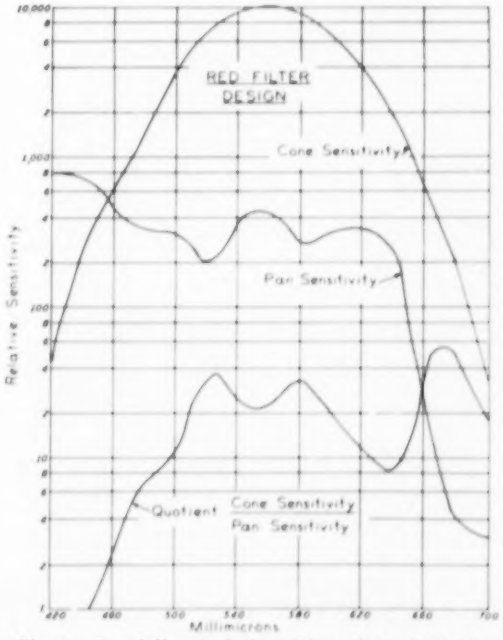

Fig. 2. A red filter is designed from data which takes advantage of the eye sensitivity and the fact that most black-white panchromatic materials fall off in sensitivity beyond 660 millimicrons.

the fact that most black and white panchromatic materials fall off in sensitivity beyond 660 millimicrons. A red filter of this type would give maximum visibility and film safety. This filter is being used in darkroom hallways at Ansco so persons not fully adapted will still have useful vision.

Filters may also be designed by taking advantage of gaps which may occur in the sensitivity of the film. As an example of this, a safelight filter for use with color print material can be designed as follows:

The spectral sensitivity of this type print material is generally as shown in Figure three. It will be noticed that there is a gap in the sensitivity around 580 millimicrons which is of lower sensitivity than the gap at 500 millimicrons. Following the same procedure as in the case of the green filter, a check on the spectral sensitivity of the cones and the spectral sensitivity of the color print material will reveal that the immediate vicinity of 580 millimicrons is the most efficient wave-length range for the peak of a safelight filter for color print material. This filter would be greenish-yellow in color and the opacity curve is shown in Figure three. This filter permits a higher visual illumination than a panchromatic green filter for equal safety factors.

Safelight filters are interesting items for the physicist to design but before their use becomes a reality, the dyestuffs and polymer chemists have to contribute their knowledge. It is preferred to manufacture these filters with cellulose acetate as a binder for the dyes. There are several reasons for choosing cellulose acetate over water soluble media such as gelatin. Among these reasons are (a) water and mold resistant properties and (b) ease of handling without danger of damaging the surface. Cellulose acetate also permits the use of spirit soluble dyes, of which there is a large selection containing many hues. These dyes also have excellent color stability.

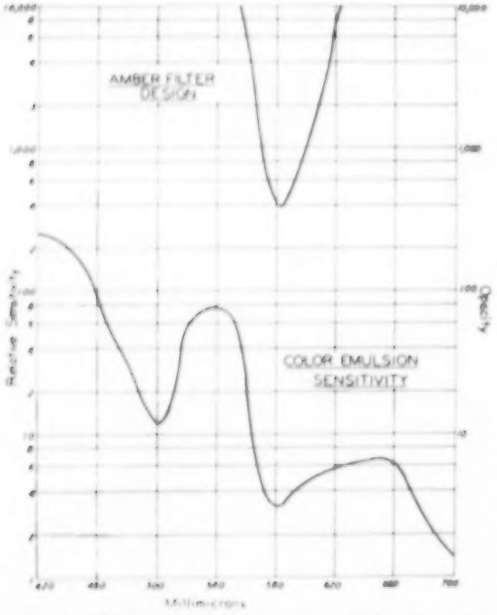

Fig. 3. The sensitivity curve of a typical color printing material. The gap at 580 millimicrons permits the use of an amber filter.

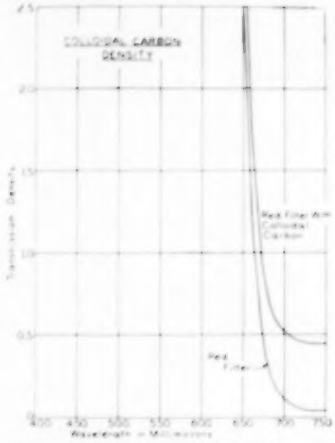

Fig. 4. The density of a safelight filter can be controlled by adding colloidal carbon to the filter formula. The hue of the filter is not disturbed.

In some cases it has been found necessary to increase the overall density of the filter without disturbing the color to any great degree. A careful control of the density of the filter can be maintained by adding a minute amount of colloidal carbon[1] to the filter mix. Figure four shows density curves of a red filter with and without colloidal carbon. It has also been common practice to use diffusing paper together with the safelight material to eliminate hot spots due to the source and to obtain a more uniformly illuminated field. A change in the ratio of the diffuse to the specular component of the transmitted light can be affected by coating the surface of the filter with a matte plastic spray.[2] This produces the same effect as the diffusing paper without the inconvenience of handling a separate item.

In general, it can be seen that the major considerations for the design of safelight filters are as follows: the response of the eye, the level of illumination, the spectral sensitivity of the material being handled, the use of dyes with proper spectral and solubility characteristics, and finally a suitably rugged casting medium.

Particular appreciation is expressed to Lloyd Bostwick of the Ansco Development Laboratories for his assistance in preparing experimental safelight filters.

1. "Dag" dispersion No. 154, marketed by Acheson Colloids Corp., Port Huron, Mich.
2. "Crescent Matton," marketed by Crescent Portrait and Frame Co., 14068–70 Euclid Ave., E. Cleveland, Ohio.

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